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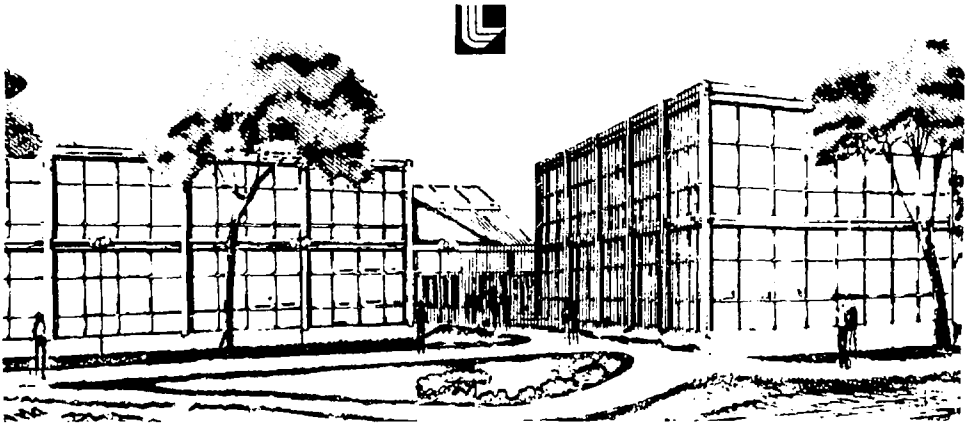

CRYOGENIC IMPLICATIONS FOR DT

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Summary

We are currently compiling cryogenic hydrogen data for magnetic fusion engineering. Many physical properties of DT can be extrapolated from H_2 and D_2 values. The phase diagram properties of the D_2-DT-T_2 mixture are being measured. Three properties which will be greatly affected by tritium should be measured. In order of their perceived importance, they are: 1) solid thermal conductivity, 2) solid mechanical strength, and 3) gaseous electrical conductivity. The most apparent need for DT data is in Tokomak fuel pellet injection. Cryopumping and distillation applications are also considered.

Introduction

The fusion fuel that ignites at the lowest temperature is DT; i.e., a mixture of the two isotopes of heavy hydrogen. The DT may be liquified or frozen at several stages in Tokomak operation. First, a fuel pellet may be fired at high speed through the magnetic field. If not initially solid, passage through the reactor chamber vacuum will freeze it. After the fusion reaction, the DT will be drawn from the reaction chamber by the 4.2 K cold of copper cryopanels. These panels will be periodically cleaned, and the DT will be distilled to D_2 and T_2 so that the proper mix is ready for the next fuel cycle.

The unique aspect about tritium, of course, is that it is radioactive, with a half-life of 12.3 years.[1] The daughter products are He^3, a beta particle, and an antineutrino. The total decay energy is 18 keV, but the beta particle can carry any amount, with 5.65 keV the mean amount.[2] The beta particle travels about 2 μm in liquid or solid, and it leaves a trail of over a hundred ion pairs behind it. Although neutrons have a more obvious ability to damage by billiard-ball collisions, ionizing radiation can cause a surprising amount of damage over time.

Of General Importance: Mixture Effects

The most obvious effect of the radiation is to transform DT into the three-component mixture: D_2-DT-T_2. This is because the tritium beta particle catalyzes the chemical reaction:

$$D_2 + T_2 \rightleftharpoons 2DT \qquad (1)$$

At room temperature and above, a 50% D - 50% T mixture produces about 50% molecular DT; at 20 K, 40%, and at 4.2 K, 9%.[3] Almost nothing is known of the reaction rate. At room temperature, the half-time to equilibrium appears to be on the order of ten minutes.[4,5] At 20 K, the H-T reaction appears to slow down to hours, as shown by the change in total pressure (DT is not sensitive enough for this method).[4] Also of interest are the rotational transitions (ortho-para) of D_2 and T_2, which may react in minutes at 20 K in the presence of a catalyst like the beta particle.[6] At Lawrence Livermore Laboratory, we are readying mass and infra-red spectroscopy to better study these reactions. An infra-red spectrum of 92% T_2 - 8% DT is shown in Fig. 1. The S(0) peak is a measure of the amount of the ground rotational state (para-T_2), and the Q and S(1) peaks measure mostly the first excited state (ortho-T_2). The smaller DT peaks are seen at higher frequency.[4] The infra-red spectrometer is a promising tool for quantitative analysis of all the isotopic and rotational hydrogen species.

There is no way to avoid the D_2-DT-T_2 mixture, because the fusion reaction itself is a near-instantaneous catalyst. Separating the tritium for magnetic fusion will be done by distillation.[5] At 25 K, for example, liquid 50% D - 50% T will fractionate to 55% D - 45% T in the vapor. Corrections of interest in distillation are the several percent deviation from Raoult's Law and the several percent increased volatility caused by the ever-present H impurity.[4,7]

The most serious potential problem occurs in freezing DT. At the 19.8 K triple point, liquid 50% D-50% T freezes to solid 48% D - 52% T. This is a small effect, but it is the accumulated fractionation that matters. The result, then of a slow freeze will be a graded composition, tritium-rich at the surface of

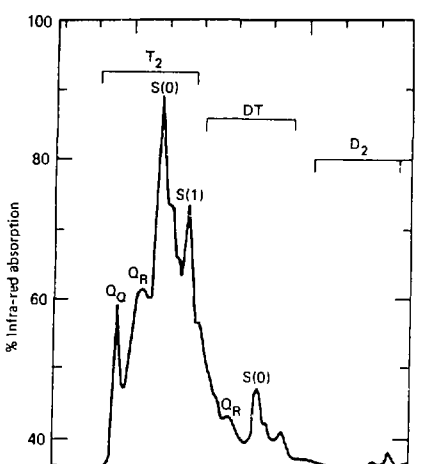

Fig. 1. Infra-Red Spectrum of Liquid 95% T_2 - 8% DT at About 21 K. The S(0) peak represents the ground rotational state; the Q and S(1) peaks measure mostly the first excited state. The Q_Q-Q_R splitting is a measure of the quasi-Debye temperature, Θ_D.

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first freezing and almost pure D_2 at the end of the freeze. A "slow" freeze is faster than one might think. For the sub-μm DT films in laser fusion targets, the extreme mobility of the liquid hydrogen[8] requires a freeze in less than 20 ms to avoid fractionation. Once frozen, the sample quickly sublimes, redistributing portions of itself to unexpected parts of the containment vessel in a crude distillation.[9] At 4.2 K, solid 50% D - 50% T will chemically equilibrate to 99% D - 1% T in the vapor phase. A final note on the solid is the possible, although unlikely occurrence of phase separation. Early arguments about this effect in solid H_2-D_2 were never quite resolved.[10]

It could be desirable to avoid mixture effects while forming and shooting the fuel pellet. This could be done by taking the center cut of the distillation column and obtaining pure molecular DT. We do not know, however, how stable this compound is (to decomposition by Eq. 1) at low temperatures.

Pellet Injection into Tokamaks

There are three properties, at least, that cannot be accurately estimated from H_2 and D_2 data. Two properties are of prime importance: solid thermal conductivity[11] and solid mechanical strength.[12] We currently lean towards the former as the first one deserving measurement, since it is needed for heat flow calculations in virtually every device that freezes DT. Radiation can only degrade this property, and the only question is how fast. Mechanical properties are important to determine the deformation of the pellet as it is accelerated. Here, there is a choice between using the soft, fresh solid or deliberately making it harder and more brittle by accumulated radiation.

The third property-electrical conductivity of DT gas--is the least important because it is needed only if electrostatic acceleration of fuel pellets is used. The tritium decay is too slow to ever self-charge a DT pellet by escape of the beta particles. The charge will have to be put on by a discharge from a needle.[13] The current and breakdown characteristics of the DT gas, which is subject to constant ionizing radiation, will affect sparking of electrodes and leakage of charge from the pellet.

We shall consider each of these three properties in the current order of importance.

Solid Thermal Conductivity

The reason why most physical properties will probably not be affected by the tritium radioactivity is the length of the half-life. The disintegration rate is 1.072×10^{15} Bq/mol T or only 2 out of 10^9 nuclei per second. At this rate, damage generally must accumulate some time to show up. The damage must also remain frozen in during this time, as in the solid, especially around 4 K. We may expect almost instantaneous annealing in the liquid.

Solid thermal conductivity is a typical solid property in that extensive radiation damage is needed to affect it. It will take hours or days--the time to produce aggregates and bubbles in the solid.

The crucial question is what the D_2-DT-T_2 mixture, plus possible rotational excitation, will do to the thermal conductivity. Data for unirradiated H_2[14] and HD[15] is shown in Fig. 2 (only one good data point exists for D_2[16]). The numbers refer to the percent of molecules in the first excited rotational state. Such excited molecules, along with dislocations and impurity atoms, all scatter phonons and lower the thermal conductivity below 10 K. The presence of the DT mixture will also cause this, and we estimate a value of about 0.2 W/m-K at 4.2 K for fresh DT. This is five orders of magnitude below that expected for a perfect crystal-never yet achieved, although a recently grown pH_2 crystal has set a new conductivity record.[17]

A few hints are to be had from 4.2 K electron spin resonance studies on solid T_2[18] and Co^{60}-irradiated solid H_2 and D_2.[19-20] The number of free electron defects saturates at about 5 ppm after 30 minutes to 30 hours. In DT, we also expect 10^{-4} mole fraction of He^3 atoms every day. Unknown, however, is the extent of local crystal breakup due to the beta particle. Such breakup should be slow to heal, even just below the triple point, as indicated by the slow molecular self-diffusion coefficient of 10^{-18} m^2/s.[21] As a pure guess, then, we estimate that the tritium radiation will lower the thermal conductivity of frozen DT from 0.2 to 0.04 W/m-K after 24 hours, and to 10^{-3} W/m-K

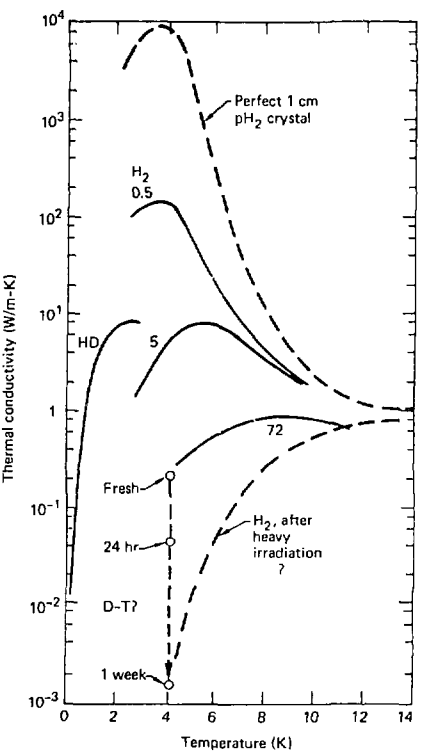

Fig. 2. Solid Thermal Conductivity of the Hydrogens. The dashed lines, which includes all DT points, are estimates. The numbers are the % of molecules in the first excited rotational state.

after a week. These values will produce unacceptable thermal gradients in DT layers thicker than 3 mm, 120 μm, and 4 μm, respectively.

A related property is the heat capacity, which will increase slightly with radiation, and then reverse sign as the radiation damage stores energy, to be released upon heating.

Solid Mechanical Properties

Pure D_2 solid has the strength of cold butter. Just below the triple point, the yield stress is 13 psi and the necking stress (where massive failure occurs) about 35 psi. At 1.4 K, the solid is only slightly stronger: the stresses are about 50 and 80 psi, respectively.[22] If we consider a single measurement on an N_2-O_2 mixture, there is no reason to expect the freshly frozen D_2-DT-T_2 to be much harder than D_2.[23] We may expect radiation hardening, which could be caused by the very first point defects formed. We are again left with a time scale of minutes to hours to ponder.

Electrical Resistivity of DT Gas

This property is instantaneously affected by radiation in all phases. Pure liquid H_2 is a hard dielectric at 10^{16} Ω-m, with charge carriers being produced only by cosmic rays. Even one part T_2 in 10^9 D_2 reduces the resistivity a hundredfold.[24] Our preliminary measurement of 5% DT - 95% D_2 is shown in Fig. 3. Resistivities are now reduced to 10^9 to 10^{11} Ω-m, or to about the range of a soft dielectric. The dashed, voltage-dependent "solid" curves are probably really gas breakdown in the cracks between the shrunken solid and the electrical plates. The efficiency of producing charge carriers drops considerably as the tritium concentration rises from 10^{-7} to 2.5%. This means the charge carriers are recombining quickly and again, the material anneals out the greater part of the damage. In the gas, however, the low density means longer lived charge carriers and perhaps the lowest electrical resistivity of any phase.

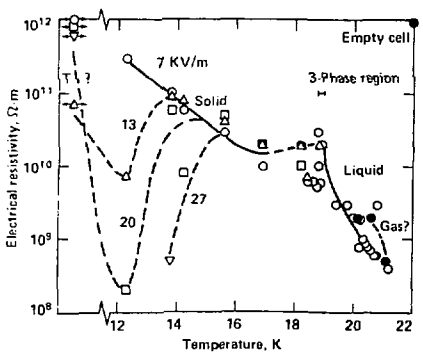

Fig. 3. Preliminary Data for Electrical Resistivity of 5% DT - 95% D_2. The dashed curves are thought to be electric breakdown of gas in shrinkage cracks between the solid and the electrical plates.

Mass Effects: Predicting DT Properties

For most properties, the only expected difference between H_2 and DT is that due to mass. It would take too long to measure all the DT properties, and it is easier to estimate them from data for H_2 (a lot), D_2 (less), HD and T_2 (very little). There is almost nothing for DT itself. Such estimates are empirical, because there is no function or process that converts the value of one isotope to that of another.

There are several excellent compendia of cryogenic hydrogen properties to start from--all but one from the National Bureau of Standards.[25-29] These sources contain little tritium data and no extrapolations (save the fluid H_2 model to 1000 atm).

We are currently preparing a compendium to complement those above. We will further develop the available data and extend estimates to DT itself.[30]

The current program to build a supersonic liquid hydrogen jet has led into little-traveled parts of the nH_2 phase diagram (100 K; 5000 atm).[31] This provides an interesting example of developing current data. We may combine molar volume and sound velocity, whether of the solid or fluid, to obtain a quasi-Debye temperature, Θ_D.[32] This is really a measure of the highest energy "lattice" vibration of a Debye solid, but it is often used as an overall parameter in equation-of-state models.[33-34] Fig. 4 shows a quick plot of available data, including the NBS fluid model.[29,35-40] This kind of plot allows rapid access to vast portions of the phase diagram for persons who must quickly calculate heat capacities. The next step is to use Θ_D to calculate the zero point energy of a molecule in its cell,[41] and from there, to work one's way to the potential energy. As an example, Fig. 5 shows the energies for solid DT at the triple point at 19.8 K.[30] We see that the zero-point energy pushes the DT molecule about half-way up in the classical potential well. Of course, all the DT data is estimated.

We close the circle by returning to the infra-red spectrum of Fig. 1. The splitting between the Q_0 and Q_R lines is a little-used but direct measure of Θ_D.[42] For the T_2 in Fig. 1, we obtain a Θ_D of 85 K for both the solid and liquid near the triple point. This shows that Θ_D is not just a function of molar volume, as is so often assumed.

Cryopumping

All present cryopumps use a 77 K baffle followed by direct condensation of the DT onto a copper panel. The helium goes on to be captured in a second stage by a molecular sieve,[5,43] ion pump,[44] or trapping in a frozen gas.[45] We have already postulated that the solid thermal conductivity and self-heating will not be important unless mm of DT are condensed or the solid layer remains for many hours. The other possible issue with solid DT concerns a possible "anomalous" vapor pressure, caused by the spike of the beta particle. Solid H_2 in the path of gas at 77 to 695 K shows a deviation above the expected vapor pressure only below 3 K and 10^{-9} torr.[46] The effect of the tritium beta particle will probably be no larger, if as great, as this. This has been recently confirmed by a mass spectrometric measurement over a thin DT film at 4.2 K.[44] The observed 10^{-11} torr total pressure compares with the expected 10^{-12} torr by extrapolation from the other isotopes.[47]

The only other possible tritium issues center on the second stage of the cryopump. Helium can be effectively pumped by trapping in an argon gas stream,[45] but H_2 and D_2 are generally ineffective.[44,45] There is a

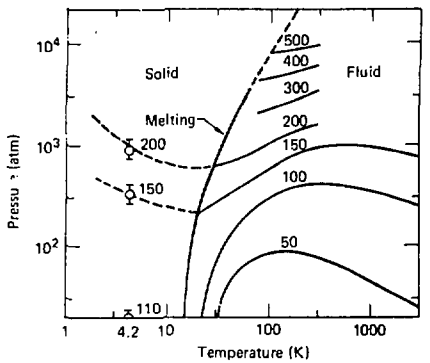

Fig. 4. The Quasi-Debye Temperature, Θ_D, of Super-Critical nH_2. Θ_D is derived from sound velocities, molar volumes, and heat capacities. The high temperature limit for the translational heat capacity is 3R for the solid and 3R/2 for the fluid.

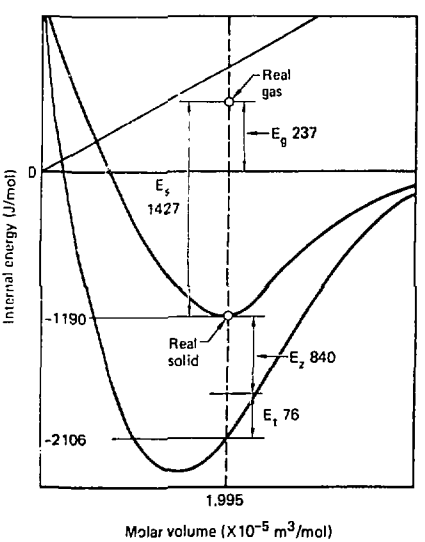

Fig. 5. Potential Energy Diagram for Solid DT at the Triple Point, 19.8 K. All numbers are estimates. The energies are: real gas (E_g), sublimation (E_s), zero-point (E_z), and thermal energy of the solid (E_t). The binding energy is -1190 J/mol, and the classical potential energy, -2106 J/mol.

faint chance that DT or T_2 with their higher mass, might dynamically trap helium, but it is not likely. There is finally the possibility of using a molecular sieve to collect DT, should an unforeseen calamity affect the copper plates. Plans are underway at ORNL to measure the amounts of H_2 and D_2 captured by adsorbents.[43] There is again a faint possibility that tritium radiation could damage the molecular sieves, although a time of days or weeks would probably be needed. A more likely problem might be the beta catalysis of an impurity reaction that poisons the adsorbent.

We see that no obvious tritium problems should affect thin cryopumped DT layers. Should thicker DT layers be used, we are led once again to the solid thermal conductivity as the main property of interest.

The Dominating Implication: Containment

The most important implication of tritium really has nothing to do with property changes. It is, instead, the containment of tritium, so that neither personnel nor environment are injured.[48-51] Time and expense are multiplied by an order of magnitude in the transition from D_2 to DT. One now has to consider glove boxes with inert atmospheres, monitors, and alarms; tritium clean-up systems; and inventory measuring equipment. It is now a world of all-metal seals, x-ray certified welded joints, double-contained transducers, miniaturized lines, and multi-thousand-dollar ballast tanks. All current certified tritium parts are made for room temperature and above. The engineering of cryogenic DT is yet to come.

Acknowledgments

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References

1. K. C. Jordan, B. C. Blanke, and W. A. Dudley, J. Inorg Nucl Chem 29, 2129 (1967).

2. W. L. Pillinger, J. J. Hentges, and J. A. Blair, Phys Rev 121, 232 (1961).

3. J. W. Pyper and P. C. Souers, The Chemical Equilibria Relating the Isotopic Hydrogens at Low Temperatures, Lawrence Livermore Laboratory, Report UCRL 52104 (1976).

4. Our data, to be published.

5. R. Sherman, Los Alamos Scientific Laboratory, Los Alamos, NM, private communication (Sept., 1977).

6. J. W. Pyper and C. K. Briggs, The Ortho-Para Forms of Hydrogen, Deuterium, and Tritium: Radiation and Self-Induced Conversion Kinetics and Equilibria, Lawrence Livermore Laboratory, Report UCRL 52278 (1977).

7. R. H. Sherman, J. R. Bartlit, and R. A. Briesmeister, Cryogenics 16, 611 (1976).

8. D. E. O'Reilly and E. M. Peterson, J Chem Phys 66, 934 (1977).

9. T. M. Henderson, R. B. Jacobs, and R. J. Simms, "Cryogenic Pellets for Laser-Fusion Research-Theoretical and Practical Considerations," preprint, presented at the 1977 Cryogenic Engineering Conference, Boulder, Colo., Aug. 2-5, 1977.

10. D. White and J. R. Gaines, J Chem Phys 42, 4152 (1965).

11. R. J. Turnbull and K. Kim, University of Illinois, Urbana, private communication (Oct., 1977).

12. S. Milora, Oak Ridge National Laboratory, Oak Ridge, TN, private communication (Sept. 1977).

13. J. P. Woosley and R. J. Turnbull, Rev Sci Instr 48, 254 (1977).

14. R. W. Hill and B. Schneidmesser, Z. Phys Chem., Neue Folge 16, 257 (1958).

15. J. H. Constable and J. R. Gaines, Phys Rev 8B, 3966 (1973).

16. R. W. Hill and B. Schneidmesser, Bull. Inst. Int. Froid, Annexe 2, 115 (1956), cited in Ref. 15.

17. J. R. Gaines, the Ohio State University, private communication (Oct., 1977,.

18. J. Lambe, Phys Rev 120, 1208 (1960).

19. L. A. Wall, D. W. Brown, and R. E. Florin, J Phys Chem 63, 1762 (1959).

20. D. W. Brown, R. E. Florin, and L. A. Wall, J. Phys Chem 66, 2602 (1962).

21. F. Weinhaus, H. Meyer, and S. M. Myers, Phys Rev 7B, 2960 (1973).

22. D. N. Bol'shukin, Y. E. Stetsenko, and L. A. Alekseeva, Soviet Physics - Solid State 12, 119 (1970).

23. I. C. Trepp, "The Hardness of Solid Nitrogen, Oxygen, Argon, and Nitrogen-Oxygen Mixtures," Schweiz Arch angew Wiss u Tech 24, 191 (1958); cited in Chem Abstracts 53, 21e (1959).

24. W. L. Willis, Cryogenics 6, 279 (1966).

25. H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Research Nat Bur Standards 41, 379-475 (1948).

26. R. Prydz, The Thermodynamic Values of Deuterium, National Bureau of Standards, Rept. 9276 (Washington, D.C., 1967).

27. B. N. Esel'son, Yu. P. Blagoi, V. N. Grigor'ev, V. G. Manzhelii, S. A. Mikhailenko, and N. P. Neklyudov, Properties of Liquid and Solid Hydrogen (Israel Program for Scientific Translations, Keter Press, Jerusalem, 1971).

28. H. M. Roder, G. E. Childs, R. D. McCarty, and P.E. Angerhofer, Survey of the Properties of the Hydrogen Isotopes below Their Critical Temperatures, National Bureau of Standards, Tech. Note 641 (U.S. Government Printing Office, Washington, D.C., 1973).

29. R. D. McCarty, Hydrogen: Its Technology and Implications. III. Hydrogen Properties, K. E. Cox and K. D. Williamson, ed. (CRC Press, Cleveland, 1975).

30. P. C. Souers, Cryogenic Hydrogen Data Pertinent to Magnetic Fusion Energy, Lawrence Livermore Laboratory, Report UCRL, to be published (1978).

31. R. Cooper, High Pressure Tokamak Fuel Injector, Physics International, Rept. PIP-1847 (San Leandro, CA., March 1977).

32. W. R. Wanner and H. Meyer, J. Low Temp. Phys. 11 715 (1973).

33. M. Van Thiel and M. Wasley, Compressibility of Liquid Hydrogen to 40,000 Atmospheres and 100°K, Lawrence Radiation Laboratory, Rept. UCRL 7833 (1964).

34. M. Van Thiel, L. B. Hord, W. H. Gust, A. C. Mitchell, M. D'Addario, K. Boutwell, E. Wilbarger, and B. Barrett, Phys Earth Planet Int. 9, 57 (1974).

35. J. W. Stewart, Phys. Chem. Solids 1, 146 (1956).

36. R. D. Goodwin, Cryogenics 2, 353 (1962).

37. G. Ahlers, J. Chem Phys. 41, 86 (1964).

38. W. Van Dael, A. Van Itterbeek, A. Cops, and J. Thoen, Cryogenics 5, 207 (1965).

39. R. L. Mills, D. H. Liebenberg, J. C. Bronson, and L. C. Schmidt, J Chem Phys 66, 3076 (1977).

40. D. H. Liebenberg, R. L. Mills, and J. C. Bronson, Thermodynamic Properties of Fluid nH2 in the Range 75-300 K and 2-20 Kbar, Los Alamos Scientific Laboratory, Rept. LA-6645-MS (April, 1977).

41. J. E. Mayer and M. G. Mayer, Statistical Mechanics (John Wiley, New York, 1940), p. 251.

42. H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, Can. J. Phys. 38, 176 (1960).

43. J. Watson, Oak Ridge National Laboratory, Oak Ridge, TN, private communication (Sept. 1977).

44. H. Halama and T. S. Chou, Brookhaven National Laboratory, Upton, L.I., N.Y., private communication (Sept., 1977).

45. T. Batzer, Lawrence Livermore Laboratory, Livermore, CA., private communication (Sept. 1977).

46. T. J. Lee, L. Gowland, and V. C. Reddish, Nature Phys Sci 231, 193 (1971).

47. P. C. Souers, C. K. Briggs, J. W. Pyper, and R. T. Tsugawa, Hydrogen Vapor Pressures from 4 to 30 K: A Review, Lawrence Livermore Laboratory, Rept. UCRL 52226 (1977).

48. T. B. Rhinehammer and P. H. Lamberger, Tritium Control Technology, Mound Laboratory, Rept. WASH-1269 (U. S. Government Printing Office Washington, D.C., Dec. 1973).

49. P. D. Gildea, "Containment and Decontamination Systems Planned for the Tritium Research Laboratory Building at Sandia Laboratories, Livermore," Proceedings International Conference Radiation Effects and Tritium Technology for Fusion Reactors, Gatlinburg, TN, Oct. 1-3, 1975; Rept. CONF-750989 (National Technical Information Service, Springfield, Va., March, 1976), III, 112-128.

50. H. J. Garber, "TFTR Tritium Handling Concepts," reference 49, III, 347-395.

51. R. T. Tsugawa, D. Fearon, P. C. Souers, R. G. Hickman, and P. E. Roberts, "A Secondary Containment System for a High Tritium Research Cryostat," reference 49, IV, 226-235.