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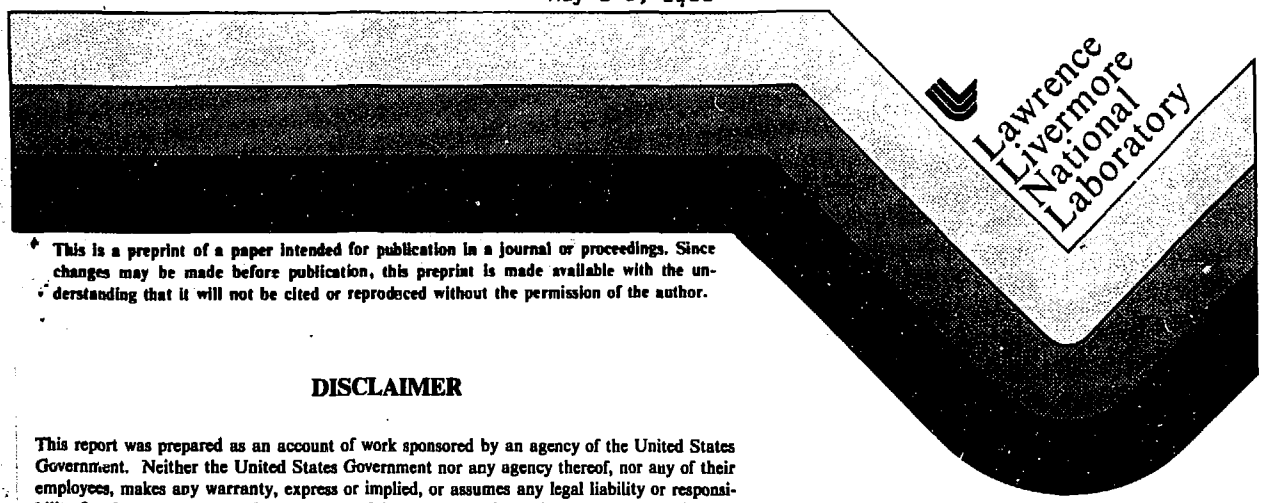

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SYNTHESIS AND STABILITY OF LIQUID MOLECULAR DT*

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ABSTRACT

Regular equimolar deuterium-tritium is a mixture of 25 mol% T_2-50% DT-25% D_2. We have synthesized molecular DT of greater purity by the reaction:

$$LiT + CH_3OD \rightarrow DT + LiOCH_3$$

run at 243 K. With both the alcohol and reactor-to-cryostat transfer lines at room temperature, we obtain 88 mol% DT purity. By cooling the alcohol and holding the transfer lines at 80 K, the yield rose to 95% DT. The DT disproportionated to D_2 and T_2 with a 1/e-time constant of about 100 hours in the liquid at 20.5 K. Nuclear magnetic resonance data showed that the eventual T_2-DT-D_2 equilibrium is probably a "hot-atom" one.

Nuclear spin polarization of frozen deuterium-tritium (D-T) offers the exciting possibility of creating a fusion fuel of high cross-section.[1] Needed for nuclear polarization is a long triton polarization memory time. Unfortunately, this is usually short in solid hydrogen because the free molecular rotation takes energy from the nuclei. Frozen HD, however, has a long proton relaxation time, after almost all J=1 H_2 (the metastable first excited rotational state) is removed by slow decay to the J=0 state.[2-4] We have previously suggested following the same path for solid D-T by using molecular DT with as little J=1 T_2 as possible.[5] An efficient approach would be to use cryogenic distillation, but we do not have the funds for this method. We here explore an alternate chemical route to enriched DT synthesis.

Before HD was available commercially, it was made in enriched form by the chemical reaction

$$LiAlH_4 + 4D_2O \rightarrow LiOD + Al(OD)_3 + 4HD \qquad (1)$$

with the best achieved yields of 97 to 98 mol% HD.[6-9] We have used this same procedure for DT with the reaction

$$LiT + CH_3OD \rightarrow CH_3OLi + DT \qquad (2)$$

Lithium tritide is used, because it can be made simply from the elements. Lithium aluminum tritide would have to be made with a tritiated solvent.

We first consider the lithium tritide. The Li^7 was from Oak Ridge and was of 99.99% purity. The tritium gas was from Savannah River and was of 99.49% purity. The synthesis was carried out in an Armco iron crucible in a doubly-contained stainless steel vessel. The crucible was first fired with ultra-pure H_2 gas at 970 K for 5 hours. The lithium metal was added, was vacuum-melted, pumped at 10^{-3} Pa at 770 K for 12 hours, and was then pumped on overnight at 370 K. Tritium was next added, and the reaction with lithium began at about 1000 K, with sufficient speed at 1020 K. The temperature was then lowered to 870 K and the tritide was annealed for 9 hours under 0.16 MPa torr of tritium gas. The resulting black solid (because of radiation-caused color centers) was ground and loaded into the DT-synthesizer vessel while in an argon atmosphere.

The schematic for the entire synthesis system is shown in Fig. 1, with arrows to show the path of the molecular DT. There are three main sections: the 243 K reactor, the transfer lines to the cryostat and the cryostat. The reactor vessel is a stainless steel can containing an Armco iron liner containing the ground lithium tritide. The reactor vessel was maintained at 243 K by constant addition of liquid nitrogen which vaporized. The deuterated methyl alcohol (Fluka; purity 99.9% with less than 0.2% H_2O + D_2O) sat initially above the reactor at room temperature. The alcohol came originally in a sealed ampoule, which was broken in an argon-filled glove box. The alcohol was transferred to a glass storage jar with a rubber septum, which was stored in dry argon. The alcohol was sucked out with a hypodermic needle, which was mounted on the reactor. In later runs, a 0.3 m length of 3 mm internal diameter

stainless steel tubing passing through a Dry Ice bed was added in order to precool the alcohol on its way to the reactor.

The transfer line connected the reactor to the cryostat, with an expansion volume at 77 K to trap alcohol vapor. The line also ran upward to a transducer, a sample bottle, another alcohol trap and a uranium getter bed. In the later runs, the transfer line system was wrapped with copper refrigeration lines held with braided copper ground straps and finally wrapped with aluminum foil. In this design, liquid nitrogen was passed through the copper lines to cool the transfer line to about 80 K. The length of the transfer line was a long 2-1/2 m, and it connected to both the infrared and nuclear magnetic resonance spectrometer cells.

The sample cell was inside a liquid helium cryostat and was held at 21 K to receive the DT product as the liquid.

The alcohol was added over about 20 to 30 minutes so that a four-times excess of alcohol over tritide was used. The 6 to 8 ml of alcohol was added in increments of 0.5 to 2 ml each. The reaction with lithium tritide was exothermic and the reactor rose to as high as 293 K. With room temperature alcohol, the time to recover to 243 K was several minutes; with cooled alcohol, it was about fifteen seconds.

The liquid product was analyzed by a combination of collision-induced infrared spectroscopy, which has already been described,[10] and mass spectroscopy. In the first four runs, the lithium tritide was also analyzed. It was first decomposed with liquid tin at 770 K according to the reaction:

$$2LiT + Sn \rightarrow T_2 + Li_2Sn. \qquad (3)$$

The residual tritium was analyzed with a Varian CH5 magnetic sector mass spectrometer. The results of the eight syntheses are listed in Table 1, with the mol % DT being the immediate measure of success. In order to lengthen the triton polarization memory time, the important variable is the ratio $([DT] + [HT])/[T_2]$.[1]

Runs #2 through #4 used a room temperature transfer line. After run #3, we started careful washing of all parts of the synthesis vessel with distilled water to remove the $LiOCH_3$ from the previous run. The vessel parts were reassembled and baked at 510 K for two days under a high vacuum. The room temperature transfer and alcohol runs are best illustrated by runs #3 to #5 with an average yield of 88%. We then added cooled alcohol and transfer lines while retaining the careful cleaning. The average yield of runs #6 to #8 rose to 95%. The reason for cooling all system parts is to slow down the wall-catalyzed exchange reaction

$$2DT \rightleftharpoons D_2 + T_2 \qquad (4)$$

In every case but one, the lithium tritide was used after no more than a one-day wait after either synthesis or an anneal at 1070 K under tritium. The exception was #7, where the LiT had been stored one month at 243 K. It is well known that radiation damage produces internally trapped bubbles of T_2 and He^3.[11,12] We feared that the trapped T_2 would lower the yield, and the 93% result is indeed lower than the 95% average. Worse yet, the He^3 blocked the cryostat input line and allowed the cell to fill only 2/3-full.

We next consider the stability of the molecular DT according to Eq. 4 in the presence of the tritium radioactivity. We had previously mixed D_2 and T_2 and observed the reaction by infrared spectroscopy for up to 45 hours. In these short runs, we obtained a time constant of 160 to 190 hours for exchange in the solid at 9 to 19 K and the liquid from 20 to 23 K.[13] These time constants assumed a "hot-atom" equilibrium, i.e., that an equimolar D-T mixture will seek the high temperature equilibrium of 25% T_2-50% DT-25% D_2. That this appears indeed to be true is shown in Fig. 2, which displays nuclear magnetic resonance data in solid equimolar T_2-DT-D_2. The height of the free induction decays (FID)[14] at 30 MHz are shown. The initial decay marks the conversion of J=1 T_2 to J=0 T_2. Then, the triton in the DT (plus constant residual J=1 T_2) gives a signal that is constant with time. These samples were cooled from room temperature in a matter of minutes and so should have a high-temperature equilibrium, i.e., about 50% DT. At 6, 10 and 20 K, the thermal equilibria are 18, 31 and 40%, respectively.[15] No decay in the n.m.r. signal height is seen over 120 hours. We conclude that the 50% DT, which gives almost all of the n.m.r. signal, remains 50% during the length of our experiments.

We observed DT sample #3 for 140 hours in the liquid at 20.5 K. The beginning and ending infrared runs are shown in Fig. 3, and we note the T_2 and D_2 signals growing in. The method of measuring composition by infrared and mass spectroscopy has been described.[10] We define the reaction parameter Y by

$$Y = \frac{[DT]_0 - [DT]}{[DT]_0 - [DT]_\infty} \qquad (5)$$

The subscript "o" indicates time zero, "∞" is at long time and no subscript means time t. The function Y will decay from 1 to 0, as shown in Fig. 4, where we show both possible equilibria. For the expected hot-atom equilibrium, $[DT]_\infty$ = 49.4% and the 1/e-time constant is 100 hours. If the thermal equilibrium exists, then $[DT]_\infty$ = 39.9% and the time constant is 140 hours. These time constants agree with the earlier data derived from short runs with D_2-T_2.[13]

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Table 1. Particulars of the enriched-DT syntheses. The average product from the room temperature reaction-line runs was 85 mol% DT; with cooled alcohol and transfer lines, it rose to 93%.

Run	LiT Used(g)	Time To Infrared Analysis (Min)	Alcohol Line to 243 K Reactor	Reactor-to-Cryostat Line	Tritide Mol% LiH	LiD	LiT
#1	0.303	19	295 K	80 K	2.7	1.5	95.8
#2	0.314	33	295 K	295 K	5.2	1.5	93.3
#3	0.299	26	295 K	295 K	1.3	0.7	98.0
#4	0.410	80	295 K	295 K	0.6	1.4	98.0
#5	0.271	54	295 K	295 K	1.3	0.4	98.3
#6	0.300	62	195 K	80 K	1.0	0.2	98.7
#7	0.310*	57	195 K	80 K	0.8	0.2	99.0
#8	0.333	53	195 K	80 K	1.5	0.3	98.2

	Product Mol%					
Run	T_2	DT	D_2	HT	HD	Ratio $\frac{(DT+HT)}{T_2}$
#1	0.5	92	4	1.7	1.8	180
#2	2	80	7	5	6	40
#3	4	87	7	1	1	20
#4	3.5	88	5.5	1.5	1.5	25
#5	2.4	90	5.4	1.1	1.2	40
#6	0.9	95	3.1	0.6	0.6	100
#7	1.2	93	4.2	0.7	0.7	80
#8	0.5	96	2.1	0.7	0.7	190

*Not annealed

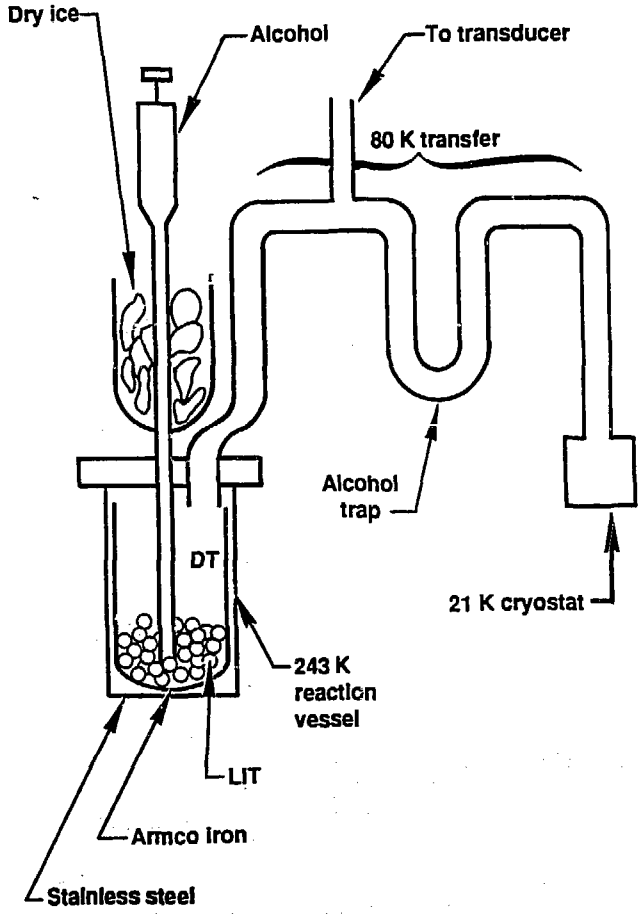

Fig. 1. Schematic of the molecular DT synthesis system.

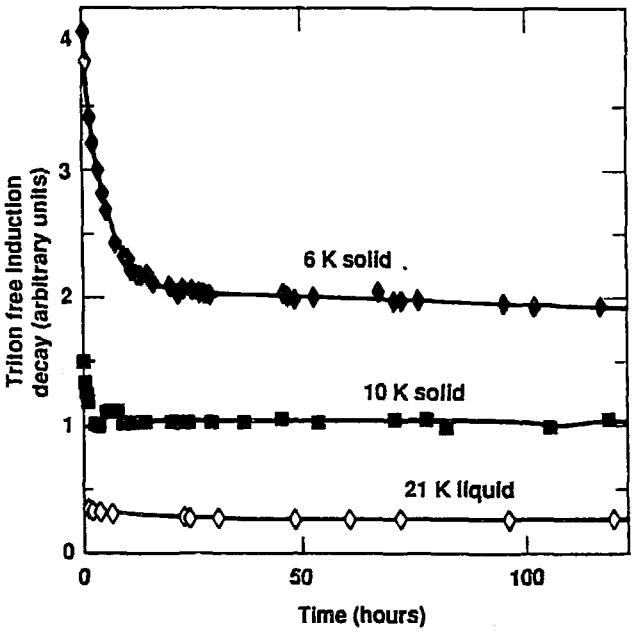

Fig. 2. Nuclear magnetic resonance signal from solid and liquid T_2-DT-D_2. The sample comes from room temperature with 50% DT, does not appear to change with time.

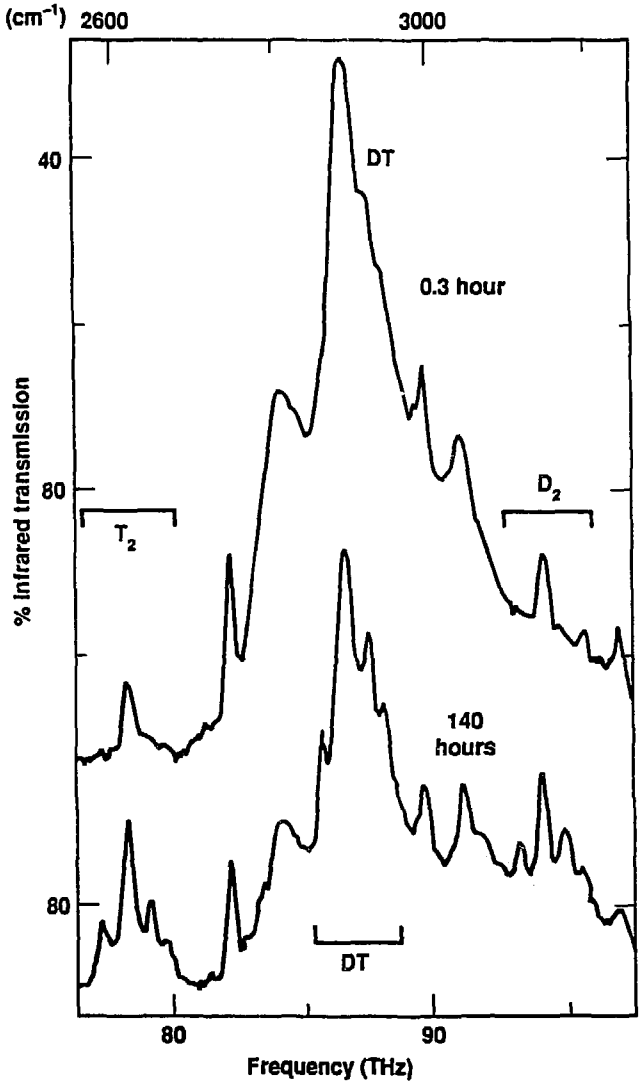

Fig. 3. Radiation-induced decomposition of DT to D_2 and T_2 in the liquid at 20.5 K. There is 87% DT at the start and 57% at the end.

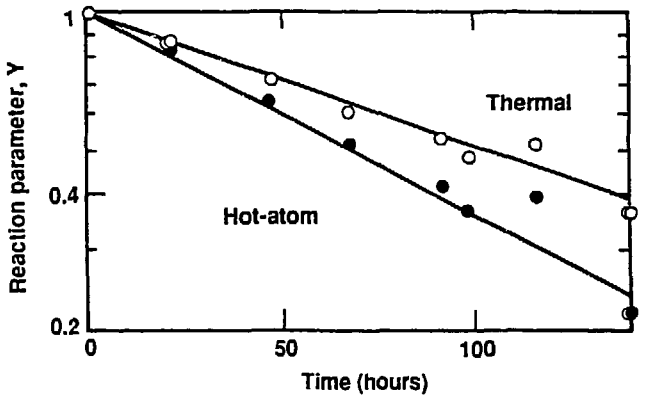

Fig. 4. Decay of enriched liquid DT at 20.5 K caused by radiation-induced chemical exchange. The results according to two possible equilibrium constants are shown, with the hot one being more probable.