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REACTION RATES FOR THE FORMATION OF DEUTERIUM TRITIDE FROM DEUTERIUM AND TRITIUM

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ABSTRACT

The rates of formation of DT in a mixture of D_2 and T_2 have been measured as a function of initial T_2 concentration, pressure, temperature, and methane concentration in a stainless steel reaction container which had been treated to inhibit protium ingrowth. An attempt has been made to explain the experimental results on the basis of ion-molecule chain reactions. Some of the observations are consistent with a gas-phase ion, ground-state molecule reaction, but some of the more interesting observations require more complicated models. The addition of excited state molecules or heterogeneous catalytic effects are possibilities that will need further experiments for confirmation.

INTRODUCTION

A program to measure the reaction rates for the production of DT in deuterium and tritium mixtures as a function of pressure, temperature, T_2 concentration, and impurity content is under way at this laboratory. We have reported¹ measurements at 295 K. There were very few reaction rate measurements for the D_2+T_2 system to be found in the literature. The only other measurements of the β induced reaction of D_2+T_2+2DT are those of Pyper, et al.² using initial T_2 concentrations of 27, 45 and 75%. We have found that the reaction can be represented

by the first order differential equation in time of Dorfman and Matraw.³ The measurements of Pyper, et al differed from the present ones in that the time dependence of the D_2 , T_2 and 1-DT concentrations required three rate constants k_1 , whereas in the present measurements the three quantities¹ can be represented by very nearly the same k .

Early measurements of the reactions H_2+T_2+2HT and H_2+D_2+2HD with a trace of T_2 present to produce the catalyzing energy were made by Dorfman, et al.³⁻⁵ They found that the reaction, which they attributed to a free radical-molecule chain-reaction, was described as first order in time. Dorfman and Shipko⁴ showed that their yields could be increased by producing a cleaner system and that, with a very clean glass system and low radiation intensity, yields as high as 2×10^4 molecules per 100 eV could be produced. In one experiment with a high T_2 concentration of 30%, which is comparable to the present experiments, a yield of 4.7×10^3 (HT) molecules per 100 eV was produced.

Thompson and Schaeffer^{6,7} irradiated H_2+D_2 mixtures with fast electrons and α particles to catalyze the reaction. They proposed that the fast electrons formed ions through the processes

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The exchange would then be of the form

The chain would stop when the charge was passed to a species which would not form HD. They found that small amounts of the Kr and Xe nearly stopped the reaction, whereas He, because of its high ionization energy, had very little effect on the reaction rate. Thus, they proposed that the reaction was an ion-molecule chain.

The present experiments were analyzed in terms of an ion-molecule reaction similar to that of Thompson and Schaeffer. It was shown¹ that the presence of CF_4 in the T_2+D_2 mixture acted as an inhibitor for the reaction. It was inferred from the measurements, where of the order of 100 ppm T_2O was present, that T_2O at this concentration is not an inhibitor. It was found that increasing the CF_4 concentration decreased the reaction rate such that $1/k$ is proportional to the CF_4 concentration, indicating a gas phase reaction. Increasing the initial T_2 concentration produced dramatically different effects depending on whether or not CF_4 impurity was detected in the mixture. With approximately 100 ppm CF_4 present, the reaction rate increases linearly with increasing initial T_2 concentration. When no CF_4 is detected, the reaction rate increases nearly exponentially with increasing initial T_2 concentration.

In the following, a steady state kinetic ion-molecule model will be applied to these observations. It will be seen that some of the more interesting observations will require a more complicated model, involving excited state molecules or heterogeneous catalytic effects in the protium free stainless steel mixing cell. The temperature dependence of the reaction for 30% initial T_2 will be given for two cases; first, where no CF_4 was detected in the T_2

samples, and then where approximately 120 ppm CF_4 was present in the T_2+D_2 mixture in the temperature region from 77 to 400 K. Talrose and coworkers⁸ have measured the temperature dependence of the B catalyzed H_2+D_2 reaction in the same temperature region and found k to decrease as the temperature is decreased. They attributed this decrease to an increasing of the ion cluster size as the temperature is decreased. Near 400 K H_3^+ was assumed and the size increases to H_{11}^+ at 77 K. The present temperature dependence of the D_2+T_2 reaction will have practical application to the handling of pure deuterium-tritium mixtures.

To conclude, we show the effect of doing the reaction in the stainless steel mixing cell in the presence of a small magnetic field of a few hundred gauss. These results point the way to a new set of experiments using cells constructed from glass, untreated stainless and gold plated stainless.

EXPERIMENTAL

The reaction rates were measured in a specially constructed stainless steel mixing cell. The cell was fabricated and treated [by Quantum Mechanics, Inc.⁹] to produce a protium free and passivated surface. A detailed description of the cell is given in Ref. 1. A diagram of the cell and filling system is reproduced in Fig. 1. The lower pressure component of the mixture was introduced first; then the higher pressure component was introduced to prevent back streaming into the lower pressure storage cylinder. The gas enters through a short cylinder at right angles to the filling capillary to facilitate mixing. The first sample was usually taken 3 or 4 min after the mixing started and the second sample 3 or 4 min later. The mixing was 97% complete after the first sample and 100% complete after the second sample. Samples were taken over a period of several hours to produce a Q vs. t line where

Fig. 1 - Diagram of mixing cell. Pressure transducers are represented by P_1 . Gas enters cell through open cylinder at right angle to capillaries.

$$\ln Q = \ln 1 - \frac{DT(t) - DT(o)}{DT(\infty) - DT(o)} = kt. \quad (3)$$

The mass spectrometer system and the accuracy of the capillary sampling analyses has been described in detail elsewhere.¹⁰

Impurity analysis of the gas samples was done with a gas chromatograph for the initial T_2 gas. In lots in which there was no detectable CT_4 , there were no chemical impurities greater than 10 ppm other than 3He . As the experiments progressed the 3He concentration increased to up to 4%. After mixing the 3He concentration was of the order of 1% and had little effect on the reaction rate. The isotopic impurities in the initial mixtures was normally 0.02% HD from the D_2 and 0.3 to 0.4% DT in the T_2 .

The temperature dependence was measured by inserting a shield between the mixing cell and the liquid nitrogen dewar and winding the cell with a heater wire connected to a proportional controller. The dewar was then filled with liquid N_2 or dry ice. The temperature, measured with the platinum thermometer, could be controlled easily to within 0.5 K. The original 30% T_2 measurements at 295 K were done at a pressure of 300 torr. The low temperature measurements were done at lower pressures so that the density of the samples constant over the temperature range.

A permanent annular magnet with an outer diameter the size of the mixing cell and a field strength of 500 gauss at the center of the circle was brought up to the bottom of the mixing cell during a room temperature run which led to a new series of experiments.

RESULTS

1. Dependence of Reaction Rate on T_2 and CT_4 Concentrations

It was previously shown¹ that there was a marked difference in the dependence of the DT reaction rate on the initial T_2 concentration depending on whether or not CT_4 was detectable, i.e., greater than 10 ppm, in the T_2 . Another way to express the reaction rate is in terms of the yield,¹¹ $G = (100/w)(M/N)$, where w is the energy to produce an ion pair, 35.6 eV,¹² M the number of DT molecules produced in the initial unit time, and N the number of ion pairs per unit time. The measured reaction rate at 295 K as a function of initial T_2 concentration is shown in Fig. 2. With 120 ppm CT_4 present, the increase in k is linear in T_2 . In Fig. 3, this behavior is represented by a parabolic dependence of G on T_2 ; i.e., $G \propto T_2^2$. The difference between k with no CT_4 observed and 120 ppm CT_4 is represented in Fig. 2 by Δk . When Δk is plotted as a function of initial T_2

Fig. 2 - Measured reaction rate as a function of initial T_2 concentration for two cases: Δ no detectable CT_4 impurity, $\bullet$ $CT_4 = 120$ ppm.

concentration, as shown in Fig. 4, a very good exponential results between 30 and 90% T_2 . An exponential dependence indicates that increasing the energy due to β decay in the mixture is producing a cooperative way of forming DT.

A kinetic model was formulated to try and explain the variety of observations seen in the formation of DT. The first step was to calculate ion densities produced in pure T_2 by the β decay energy. Then, reactions with the impurity CT_4 were added. Finally, the chain reaction of the form of Equation (2) was added with the addition of D_2 to the mixture. In Table I a set of reaction equations is given where the rate constants, k_i , have been found in the literature. The ion densities were first calculated for pure T_2 . The reaction represented by k_3 in

Fig. 3 - Reaction rate yield as a function of initial T_2 concentration in two limiting cases; Δ and $\bullet$, no detectable CT_4 impurity; and $\bullet$, $CT_4 = 120$ ppm.

Fig. 4 - Dependence of Δk on initial T_2 concentration. The definition of Δk is shown in Fig. 2.

Table I - CALCULATION OF ION DENSITIES IN PURE AND IMPURE TRITIUM EQUATIONS FOR STEADY STATE ANALYSIS (PURE T₂)

		Reference No.
$e^+ + T_2 \rightarrow T_2^+ + e^-$	$k_1 = 5 \times 10^{-8}$	13
$e^- + T_2 \rightarrow T + T^-$	$k_2 \sim 10^{-20}$	14
$e^- + T_2^* (v=4) \rightarrow T + T^-$	$k_3 = 2 \times 10^{-8}$	13
$T_2^+ + T_2 \rightarrow T_3^+ + T$	$k_4 = 1.2 \times 10^{-9}$	15
$T_3^+ + e^- \rightarrow T_2^+ + T$	$k_5 = 5 \times 10^{-9}$	15
$T_3^+ + e^- \rightarrow T_2^+ + T^-$	$k_6 = 1.8 \times 10^{-8}$	15
$T_3^+ + T^- \rightarrow T_2 + T_2$	$k_7 = 2 \times 10^{-7}$	13
$T + T + M \rightarrow T_2 + M$	$k_8 = 2 \times 10^{-32}$	16

ADDITION OF D₂

$T_3^+ + D_2 \rightarrow T_2 D^+ + DT$	$k_9 = 1.2 \times 10^{-9}$	17
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ADDITION OF METHANE, CT₄

$T_3^+ + CT_4 \rightarrow CT_5^+ + T_2$	$k_{10} = 5 \times 10^{-10}$	18
$CT_5^+ + T^- \rightarrow CT_4 + T_2$	$k_{11} = 2 \times 10^{-7}$	13
$CT_5^+ + e^- \rightarrow CT_4 + T$	$k_{12} = 5 \times 10^{-9}$	15

Table I involve vibrationally excited T₂. The β decay creates considerable internal energy in the gas. A search was made for a reaction that might explain the rapid increase in k with increasing T₂ in the mixture. In Reaction k₃ v=4 is a representative value for model calculations, because v can run from 1 to 14. The excited state tritium is represented by T₂^{*}.

If one assumes reaction k₃ is operative and CT₄=0, the following steady state results:

$$T_2^+ \quad ne^+ T_2 k_1 + T_3^+ e^- k_6 = T_2^+ T_2 k_4 + T_2 \quad (4)$$

$$e_3^- \quad ne^+ T_2 k_1 + e^- [T_2^* k_3 + T_3^+ (k_5 + k_6) + T_2 k_2] \quad (5)$$

$$T_3^+ \quad T_2 T_2^* k_4 = T_3^+ [e^- (k_5 + k_6) + T^- k_7] \quad (6)$$

$$T^- \quad e^- (T_2^* k_3 + T_3^+ k_6) = T^- T_3^+ k_7 \quad (7)$$

Charge neutrality requires

$$T_2^+ + T_3^+ = e^- + T^- \quad (8)$$

A value for the number of energetic electrons e⁺, which are differentiated from thermal electrons, e⁻, was given previously.¹⁹ The lifetime of e was overestimated by a factor of 40. Thus, at any time e=2.8/cc, and each electron averages 155 ionizing collisions, given ne=4.35x10²/cc, whereas the density of T₂ is 2.7x10¹⁹/cc.

From equation (4) and Table I,

$$T_2^+ = \frac{ne^+ T_2 k_1 + T_3^+ e^- k_6}{T_2 k_4} = \frac{5.9 \times 10^{14} + T_3^+ e^- 1.8 \times 10^{-8}}{3.2 \times 10^{10}} \quad (9)$$

Since in equation (5) T₃⁺(k₅+k₆) >> T₂k₂, and assuming T⁻=0, e⁻T₃⁺=ne⁺T₂{k₁/(k₅+k₆)}. Thus the maximum value of e⁻T₃⁺=2.55x10²². Then T₂⁺=3.3x10⁴ ions/cc which will be seen to be much smaller than the magnitude of T₃⁺.

Then T₃⁺, e⁻ and T⁻ becomes,

$$T_3^+ = \frac{5.9 \times 10^{14}}{e_3^- 5 \times 10^{-9} + T^- 2 \times 10^{-7}} = \frac{5.9 \times 10^{23}}{5e_3^- + 200 T^-} \quad (10)$$

$$e^- = \frac{5.9 \times 10^{14}}{T_3^+ 2.3 \times 10^{-8}} = \frac{5.9 \times 10^{23}}{23 T_3^+} \quad (11)$$

and

$$T^- = e^- \frac{1.8 \times 10^{-8}}{2 \times 10^{-7}} = 0.09 e^- \quad (12)$$

$$\text{Assuming } T_2^+ \ll T_3^+, \text{ then } T_3^+ = T^- + e^-. \quad (13)$$

Solving equations (9) through (13) gives,

$$T_2^+ = 3.3 \times 10^4, \quad e^- = 1.53 \times 10^{11} \quad (14)$$

$$T_3^+ = 1.67 \times 10^{11},$$

$$T^- = 1.4 \times 10^{10} \text{ ions/cc.} \quad (15)$$

Thus, with no excited state T_2^+ , the ratio of T^-/e^- is 0.09.

Let $X = T_2^+/T_3^+$, then T_3^+ in units of 10^{11} ions/cc is

$$T_3^+ = \frac{59}{e^-(5 + 18 + 20X)} \quad (16)$$

Then from charge neutrality

$$T_3^+ = e^- + T^- = e^-(1 + 0.09 + 0.1X) \quad (17)$$

and therefore

$$(T_3^+)^2 = 59 \frac{(1.09 + 0.01X)}{(23 + 20X)} \quad (18)$$

Solving equation (18) for given values of X reduces the equation to a quadratic in T_3^+ and still gives T_3^+ as a function of T_2^+ .

Table II shows increasing T_2^+ reduces the ratio of e^- to T^- through $e^- + T_2^+ (v=4) \rightarrow T + T^-$. Recent measurements of ion concentrations in H_2 plasmas^{20,21} indicate that the N^-/e^- ratio is between 1 and 10. Thus Reaction k_3 of Table I is a likely measure of excited state T_2^+ in tritium gas. A good experimental measure of T^-/e^- in tritium gas would be very useful.

Table II - DEPENDENCE OF ION CONCENTRATIONS
ON $T_2^+ (\times 10^{11}/cc)$

X	T_3^+	e^-	T^-	T_2^+
	(10 ¹¹ ions/cc)			
0	1.67	1.53	0.14	0
0.01	1.66	1.52	0.14	0.016
0.1	1.62	1.47	0.14	0.16
1.0	1.28	1.07	0.21	1.2
10 ¹	0.74	0.36	0.38	7.0
10 ²	0.57	0.05	0.52	57
10 ³	0.55	0.005	0.54	550
10 ⁴	0.54	0.0005	0.54	5500

A measurement of the ratio of T^- to e^- was made by Souers, et al.¹² At first, they indicated the ratio to be of the order of 100 but a subsequent analysis²² including space charge effects in their experiment showed the ratio could not be determined from the conductivity experiments. His analysis indicated that the ion density in the case of no conductivity losses was $N = [(dN/dt)/k]^{1/2}$ where $dN/dt = 1.48 \times 10^{13}$ ions/cc s and $k = 2 \times 10^{-7}$ ions/cc s, giving $N = 8.6 \times 10^9$ /cc. He uses this value of k for the recombination of H_3^+ and e^- . Based on the analysis in Table I, the recombination of T^- has this fast rate whereas the recombination of e^- is slower. Even when T^- is dominant (see Table II), the more complex set of equations (4 through 8) produces a larger value of N . Risks¹³ gives an e^- recombination rate of 5×10^{-8} which is an intermediate value. Thus, $N \sim 10^{11}$ or 10^{12} ions/cc is probable. An experiment to detect excited state T_2^+ and T_3^+ using a CARS technique is being started in collaboration with C. J. Kershner of Mound.

The principal impurity in the T_2 is methane, CH_4 . We have shown that increasing CH_4 content in the T_2 inhibits the DT reaction. Previously²³ the effect of CH_4 was calculated assuming k_{10} was of the order of 10^{-12} cc/molecule/s in analogy with the $H_3^+ + D_2 \rightarrow H_2^+ + HD$

rate.²⁴ A new measure of this rate¹⁷ shows it to be much faster with $k=2 \times 10^{-9}$. Accounting for the mass factor in the velocity, produces $k_{10}=5 \times 10^{-10}$. Using the k values in Table I, the following charge densities are found,

$$T_3^+ = \frac{5.9 \times 10^{23}}{5e^- + 200 T^- + 0.5 CT_4^+} \quad (19)$$

$$CT_5^+ = \frac{0.5 CT_4 T_3^+}{5e^- + 200 T^-} \quad (20)$$

$$e^- = \frac{5.9 \times 10^{23}}{23 T_3^+ + 20 T_2^+ + 5 CT_5^+} \quad (21)$$

and

$$T^- = \frac{18 T_3^+ e^- + 20 T_2^+ e^-}{200 T_3^+ + 200 CT_5^+} \quad (22)$$

If we assume $T_2^+ = 5 \times 10^{12}$, e^- changes very little, and the equations are simplified as follows, using concentration units of 10^{11} ions/cc

$$T_3^+ = \frac{11.8}{e^- + 40 T^- + 0.1 CT_4^+} \quad (23)$$

$$e^- = \frac{11.8}{4.6 T_3^+ + CT_5^+ + 200}$$

$$CT_5^+ = \frac{0.1 CT_4 T_3^+}{e^- + 40 T^-}$$

$$T_3^- = e^- \frac{3.6 T_3^+ + 200}{40 T_3^+ + 40 CT_5^+} \quad (24)$$

Then

$$e^- = 0.059 \text{ to } 0.058 \text{ as } T_3^+ = 0 \text{ to } 0.56, \quad (25)$$

and

$$T^- (T^- + 0.059) = 0.059 \frac{(3.6 T_3^+ + 200)}{40} \quad (26)$$

gives

$$T^- = 0.514 \text{ to } 0.513 \text{ as } T_3^+ = 0 \text{ to } 0.56. \quad (27)$$

Therefore, with $T_2 = 2.7 \times 10^{19}$ /cc, increasing the CT_4 concentration decreases T_3^+ as shown in Table III.

Table III - DEPENDENCE OF T_3^+ ON CT_4 IMPURITY
(Units of 10^{11} ions/cc)

CT_4 (ppm)	T_3^+	CT_5^+
0.01	0.563	0.0005
0.1	0.506	0.005
1.0	0.253	0.319
10.0	0.042	0.534
100.0	0.0045	0.571
1000.0	0.00045	0.576

A measure of the consistency of the reaction rates in Table I is seen in the application of charge neutrality. From equations (25) and (27), $T^- + e^- = 0.573$ is nearly equal to the 0.563 to 0.576 obtained from equations (23) and (24) for $T_3^+ + CT_5^+$. The fact that T_3^+ decreases with increasing CT_4 is consistent with the observed decrease in the rate of DT production with increasing CT_4 concentration. The decrease in T_3^+ in Table III is a consequence of the larger value of k_{10} .

Addition of D_2 to the tritium ion mixture allows the reactant ion in equation (2) to be T_3^+ , $T_2 D^+$, $T D_2^+$, or D_3^+ and we will denote it as R_3^+ . If R_3^+ is formed from T_2 in equation (1), it will be denoted as R_T^+ . If R^+ is formed from D_2 it is R_D^+ . Thus,

$$R_T^+ = \frac{T_2}{D_2 + T_2} R_3^+ \text{ and } R_D^+ = \frac{D_2}{D_2 + T_2} R_3^+ \quad (28)$$

Then the T rich R_T^+ reacts with D_2 to form DT and in the same way D rich R_D^+ reacts with T_2

with a rate k_9 given in Table I. Then the change in DT can be written as

$$\frac{dDT}{dt} = k_9 T_2 R_D^+ + k_9 D_2 R_T^+ = 2k_9 \frac{T_2 D_2}{D_2 + T_2} R_3^+ \quad (30)$$

In analogy with equations (6) and (19) the reactant R_3^+ can be written

$$R_3^+ = \frac{n_1 e_1^- (T_2 + D_2) k_1}{D_2 T_2 \left(\frac{D_2 + T_2}{D_2} k_5 + e_3^- (1+\alpha) k_3 + CT_4 k_{10} \right)} \quad (31)$$

Then equation (33) becomes

$$\frac{dDT}{dt} = \frac{2k_9 \frac{D_2 T_2}{D_2 + T_2} A T_2 k_1}{\frac{D_2 + T_2}{D_2} k_5 + e_3^- (1+\alpha) k_3 + CT_4 k_{10}} \quad (32)$$

where $A = 4.35 \times 10^2$ and $\alpha = T^- / e_3^- \cdot k_7 / k_3$. The yield G is proportional to the ratio of $\frac{dDT}{dt} / A T_2 k_1$. When the CT_4 impurity content is large, G is proportional to the quantity $D_2 T_2 / (D_2 + T_2)$ as is shown in Fig. 3. The dependence of G on T_2 with no CT_4 detectable is not represented by equation (32).

2. Dependence of k on Temperature

The temperature dependence of 30% initial T_2 mixtures was measured between 77 and 400 K in two cases. In the first case, no CT_4 was detected in the measurements. In the second set of measurements ~120 ppm CT_4 was present in each run. The results are shown in Fig. 5. The error bar at 295 K represents four determinations at that temperature with the uncertainty being in the amount of CT_4 under the mass

Fig. 5 - Temperature dependence of formation of DT from $D_2 + T_2$ in 304 stainless steel mixing chamber. Δ no impurities detected; $\bullet$ approximately 120 ppm CT_4 , + approximately 100 ppm N_2 . The error bar $\bar{\Delta}$ represents four measurements at that temperature.

spectrometer detection limit of 30 ppm in the different gas lots. A very fast region appears between 150 and 230 K. The variation observed in this region is also most likely due to undetected impurities in the samples. It will be shown that the fastest reaction at 195 K was with a new batch T_2 with $CT_4 < 10$ ppm.

Addition of 120 ppm CT_4 reduced the reaction rate at all temperatures measured. The broad resonance was reduced to a small peak below 200 K. One experiment using pure T_2 was run with 100 ppm N_2 detected in the D_2 before mixing which is represented by (+) which indicates the inhibiting effect of N_2 . The temperature dependence of the $H_2 + D_2 \rightarrow HD$ measurements of Talrose and coworkers,⁸ showed a nearly linear decrease from 300 K to 77 K on the scale of

Fig. 5. The reason for our observed resonant type of behavior is under investigation. At temperatures below the fast region the rate does not increase with increasing initial T_2 concentration²⁵ indicating the character of the reaction changes at low temperature.

The dependence of the DT reaction rate on CT_4 concentration was then measured at 193 K, in the center of the temperature resonance. The point (M) in Fig. 6 represents 100 ppm CT_4 and the point (D) represents 30 ppm CT_4 . The three points in between represent 30, 50, and 75% mixtures of these two impure T_2 samples (M and D). The largest rate at 195 K was measured using T_2 just received from the separation system with a CT_4 concentration <10 ppm as measured by a gas chromatograph. The 100

Fig. 6 - Dependence of mean time $T = 1/k$ on CT_4 concentration. The x's represent 30, 50, and 75% mixtures of D and M. The line is determined by M, $CT_4 = 100$ ppm and D, $CT_4 < 10$ ppm. The T for D then places this point at 20 ppm.

ppm and <10 ppm CT_4 points determine a line shown in Fig. 7 where $1/k$ is plotted against CT_4 concentration. The point (D) then falls at 20 ppm. The three mixtures between 20 and 100 ppm conform well to the straight line. This behavior is consistent with the gas phase calculation of T_2^+ in Table III.

3. Effect of Small Magnetic Field

Out of a sense of curiosity we brought a 500 gauss radio speaker magnet up to the mixing chamber before a room temperature run with 30% initial T_2 and held it there during the mixing. The reaction rate increased by a factor of two. The magnet was taken away, and the experiment was repeated. The fast reaction time occurred again. The magnet was brought up a second time for a third experiment and the reaction time did

Fig. 7 - Upper position of Fig. 5 with data added after bringing magnet up to mixing chamber. Δ no impurities detected before magnet experiments; $\square$ in presence of magnet, $\circ$ and $\times$ are two different lots of starting gases after magnet was removed, ∇ after degaussing cell.

not change. The results of these experiments are shown in Fig. 7. The solid triangles ($\blacktriangle$) represent experiments done before the magnet experiments. The open squares ($\square$) represent experiments with the magnet present. The circles (o) and crosses (x) represent subsequent experiments done with no magnet present after the magnet was brought near the mixing chamber. The resonance near 200 K is still present, but the structure above 220 K has been washed out. All the experiments shown in Fig. 7 were done with initial T_2 and D_2 displaying no detectable impurities. The circles (o) and crosses (x) represent two different lots of initial T_2 .

The presence of the small magnetic field appears to have changed the mixing cell surface since the increased rate at 295 K remained with different lots of gas after the magnetic field was removed. A degaussing coil was constructed so that a 500-gauss alternating field could be reduced to zero around the mixing cell. A measurement of the mean time for the reaction after degaussing was 68 min, nearly a factor of two slower than the original mean time before the magnetic field was applied to the cell.

DISCUSSION

The formation of DT by mixing D_2 and T_2 in a stainless steel container is quite complex because of the internal energy in the system supplied by the T_2 β -decay. The energy is sufficient to produce a steady state population of electron-ion pairs. The ions give rise to an ion-molecule chain reaction in which an exchange of the form $T_3^+ + D_2$ to form DT with nearly every collision. The presence of impurities other than He stops the chain when the charge transfer produces ions such as CT_3^+ and N_2T^+ which do not continue the chain. It was seen in the ion density calculations that the simple ion-molecule interaction gave rise to ion densities about two orders of magnitude larger than those measured by Souers, et al.²² This difference may arise from the fact that there are no ion

sinks on the boundaries in the calculation. The calculated decrease in T_3^+ with increasing CT_4 is consistent with the decrease in k for the production of DT. When of the order of 100 ppm CT_4 is present the production of DT is consistent with the ion-ground state molecule model.

The reaction results using pure D_2 and T_2 components are more complicated. It appeared in the variation of the initial T_2 concentration that a reaction with an isotope effect is dominant. Equation (3) in Table I represents such a reaction. Allen and Wong¹⁴ found a difference of nearly an order of magnitude in k_3 between D_2 and H_2 for $v=4$. For $v>7$, Hiskes, et al.²⁰ have found that the isotope difference disappears. The presence of vibrationally excited T_2 and D_2 changes the electron to negative ion ratio but it does not appear to effect the R_3^+ concentration. Recent measurements²⁶ of the reaction cross section of $H_3^+(v) + H_2$ does not increase with increasing v . Therefore, the similar reaction in the D_2+T_2 system does not appear to be a candidate to explain the fast reaction in the T_2 rich mixtures.

The temperature dependence of the reaction displays a very fast resonant like region between 150 and 220 K. In this region the reaction rate is limited by impurities of the order of a few ppm. In this region, the dependence on CT_4 is of the same form at 295 K. Adding 120 ppm CT_4 reduces the resonant region to a small peak at about 180 K. The experiments of Talrose, et al using H_2+D_2 do not show this fast region. Thus, it is possible that the fast reaction arises from an interaction with the mixing cell surface. The cell was etched and vacuum baked to make the measurements as protium free as possible. The etch removed Fe from the surface making the surface nickel-chrome rich. Normal 304 stainless steel is non-magnetic. Removing one component from the surface could leave the surface with a magnetic character.

The reaction rate at 295 K was changed with the application of a small magnetic field and remained changed after the field was removed even with different lots of initial T_2 and D_2 . Thus the surface has an effect on the measured reaction rates. It can be seen in Fig. 7, though, that the fast region below 220 K remains. The value of G at 200 K is the order of 10^4 . Thompson and Schaeffer⁶ have calculated that, if the surface was the only terminator of the R_3^+ chain, G would be of the order of 10^7 in his mixing cell which was nearly the same size as the one used in this work. Thus, the values of G between 2×10^3 to 10^4 observed in these experiments should be limited by gas impurities even though they may be below our level of detectability.

The reaction rate measurements in the D_2+T_2 system display a complex set of results because of the energy deposited in the gas by the β -decay. Some of the results can be explained in terms of ion-molecule reactions in a complex mixture of ions in a T_2+D_2 background. Possible surface effects still need to be separated from the gas phase reactions. Glass and gold plated mixing cells have been constructed to continue the investigation.

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