TRITIATED AMMONIA FORMATION (U)

L. K. Heung

March, 1994

Savannah River Technology Center
Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared For The U. S. Department Of Energy Under Contract DE-AC09-84SR18035

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This work was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily reflect those of the United States Government or any agency thereof.

TRITIATED AMMONIA FORMATION (U)

L. K. Heung

March, 1994

APPROVALS AND REVIEWERS

L. K. Heung

L. K. Heung, Author
Process Technology Group
Chemical and Hydrogen Technology Section

3/8/94

Date

G. S. Nichols

G. S. Nichols, Technical Reviewer
Process Technology Group
Chemical and Hydrogen Technology Section

3/8/94

Date

T. Motyka

T. Motyka, Manager and ADC
Process Technology Group
Chemical and Hydrogen Technology Section

3-9-94

Date

J. R. Knight

J. R. Knight, Manager
Chemical and Hydrogen Technology Section

3/11/94

Date

TRITIATED AMMONIA FORMATION (U)

L. K. Heung

March, 1994

Introduction

Back in 1984, when nitrogen was selected as the glovebox atmosphere for the Replacement Tritium Facility (RTF), a concern was raised as to the possibility of tritiated ammonia formation in the gloveboxes, particularly during a large tritium release. A paper by Maienschein of Lawrence Livermore Laboratory indicated that NT₃ formation in a nitrogen glovebox could be significant.¹ Walters at SRS reviewed the Maienschein paper, and with the help of literature data, derived a rate law for the formation of NT₃ from T₂ and N₂.² He concluded that the rate of forming tritiated ammonia in a nitrogen glovebox should be thousand times smaller than what was estimated by Maienschein, therefore not a problem for the RTF gloveboxes. Later in 1991 when a set of experimental data showing tritiated ammonia formation as a function of time was produced at SRS, Walters found that his rate law did not fit the data. When he increased the rate constant by a factor of 10, he was able to adjust his rate law to fit the first 200 hours of data, but not the data after 200 hours.³ In addition, his rate law did not predict equilibrium shown by the data.

Recently, the concern about tritiated ammonia formation came up again in the RTF. The question is how much tritiated ammonia can form in the mix tanks if there is nitrogen in the tanks. I have reviewed the works by Walters, and have developed a new rate equation which closely simulates the whole set of experimental data produced at SRS. This rate equation greatly improves our confidence in predicting the formation of tritiated ammonia under different conditions.

Summary

1. A rate equation that closely simulates experimental data has been developed. This rate equation can be used to calculate the formation of tritiated ammonia from different concentrations of tritium and nitrogen.
2. The reaction of T₂ and N₂ to form NT₃ is a slow process, particularly when the tritium concentration is low. The reaction requires weeks or months to reach equilibrium dependent on the concentrations of the reactants.

Model Development

The reaction between tritium (T_2) and nitrogen (N_2) to form tritiated ammonia (NT_3) is represented by the following equation:

The rate equation for the formation of NT_3 is written as:

$$\text{Rate} = \frac{d[NT_3]}{dt} = k_1 * [T_2]^3 * [N_2] - k_2 * [NT_3]^2 \quad (2)$$

where

Rate = g-mole of NT_3 /liter/hr

$[NT_3]$, $[T_2]$, $[N_2]$ are concentrations, g-mole/liter

t = time, hr

k_1 , k_2 = rate constants.

We further let

$$\text{Rate} = r \quad [NT_3] = A \quad [T_2] = Tr \quad [N_2] = N \quad K = k_1/k_2.$$

Equation (1) becomes

$$r = k_1 * Tr^3 * N - k_2 * A^2$$

Rearranging gives:

$$r / (Tr^3 * N) = k_1 - k_2 * A^2 / (Tr^3 * N) \quad (3)$$

Equation 3 defines a straight line with the dependent variable $y = r / (Tr^3 * N)$, and the independent variable $x = A^2 / (Tr^3 * N)$. The slope is $-k_2$, intersect k_1 .

With experimental data, one may calculate the values of r , Tr , N and A , Equation 3 may then be used to examine if the rate equation (Eq. 2) correctly represents the reaction. If the rate equation is correct, a plot of $y (=r / (Tr^3 * N))$ versus $x (=A^2 / (Tr^3 * N))$ must be a straight line. The slope and the y-intersect of the line will define the values of k_2 and k_1 , respectively.

Experimental Data

An experiment was conducted at SRS to study the reaction rate between T₂ and N₂ to form tritiated NT₃. The experimental details and results have been documented by Walters in Reference 3. They are briefly included here since the data will be used to examine the above rate equation.

A stainless steel container of 1.456 liter internal volume was used as the reaction vessel. A MKS Baratron Capacitance Manometer and a thermocouple, both directly inserted into the vessel, were used to measure the pressure and temperature. At time zero, 1123 torr of nitrogen and 1095 torr of tritium were charged into the vessel to start the experiment. The pressure and temperature were recorded periodically. The NT₃ concentration is calculated from the pressure and temperature using equation (4) below, which is derived according to the stoichiometry of the reaction (Appendix 1):

$$A = \frac{1}{R} \left\{ \frac{P_{to}}{T_o} - \frac{P_t}{T} + \frac{P_{tro}}{T_o} [1 - \exp(-\lambda * t)] \right\} \quad (4)$$

Where

A=[NT₃], g-mole/liter

R=gas constant, 62.4 torr-liter/g-mole/K

P_{to}=Total pressure at time zero, torr

P_t=Total pressure at time t

P_{tro}=Tritium pressure at time zero, torr

T_o=Temperature at time zero, K

T=Temperature at time t, K

λ=Tritium decay constant, 6.43E-6 hr⁻¹

t=time, hr.

The data of time, pressure and temperature, and the calculated NT₃ concentration (by equation 4) are listed in Table 1. The pressure and temperature trends are also plotted in Figure 1 to show their fluctuations. The fluctuations are quite significant and will contribute to the scattering of the rate of ammonia formation to be calculated below.

Examination of The Rate Equation

Equation (3) and the experimental data are used to test equation (2) for the rate equation. The rate of ammonia formation is first calculated from the data of ammonia concentration given in Table 1, using

$$\text{Rate} = r = \frac{\Delta A}{\Delta t} \quad (5)$$

where ΔA is the increase of NT_3 concentration in time Δt . The rate is plotted in Figure 2 as a function of time. Two of the 52 data points are obviously out of place and are discarded. The values for $y=r/(Tr^3 * N)$ and $x=A^2/(Tr^3 * N)$ are then calculated, and plotted in Figure 3. The points are rather scattered, but the trend of a straight line is clearly shown. Regression analysis gives a straight line with a slope of -0.0900 and an intersect of 1.462. Therefore the values of the constants for the rate equation (Eq. 2) are

$$k_1 = \text{intersect} = 1.462$$

$$k_2 = -\text{slope} = 0.0900$$

Equation 2 becomes:

$$\text{Rate} = \frac{d[NT_3]}{dt} = 1.462 * [T_2]^3 * [N_2] - 0.09 * [NT_3]^2 \quad (6)$$

where

Rate = g-mole of NT_3 /liter/hr

$[NT_3]$, $[T_2]$, $[N_2]$ are concentrations, g-mole/liter

t = time, hr

Equation 6, as shown in Figure 4, matches the data quite well.

One may take one more step to see if Equation 6 really fits the experimental data. The ammonia concentration as a function of time is calculated using the initial concentrations of tritium and nitrogen in the experiment. The calculated results are plotted in Figure 5 in comparison with the experimental results. They are in excellent agreement for the whole duration of 1,000 hours of the experiment. Equation 6 fits the experimental data very well indeed.

Application of The Rate Equation

Equation 6 can be used to calculate the amount of NT_3 formed as a function of time when the initial concentrations of T_2 and N_2 are known. Since it is difficult to integrate Equation 6 analytically, a numerical technique will be used here in two different cases to demonstrate its application.

(1) The first case involves the presence of nitrogen in a tritium storage tank.

Given:

Total pressure:	2.5 atm
Gas temperature:	20 °C
Initial tritium concentration:	99.8 mole%
Initial nitrogen concentration:	0.2 mole%

RECEIVED

MAY 13 1994

OSTI

Calculate:

Tritiated ammonia NT₃ as a function of time.
The maximum NT₃ that can be produced.

Solution:

In equation 6, the concentrations of T₂ and N₂ can be expressed in terms of their initial concentrations and the concentration of NT₃. After that, the equation becomes a quartic function of NT₃ concentration, and is difficult to solve analytically. But it can easily be solved by stepping up the time using numerical techniques.

At time $t=t_0=0$,

the concentrations of tritium and nitrogen in terms of g-mole/liter are:

$$[T_2]_0 = 0.998 * (2.5 * 1 / (1 * 22.4 / 1 / 273)) / (273 + 20) = 0.103781 \text{ g-mole/liter}$$

$$[N_2]_0 = 0.002 * (2.5 * 1 / (1 * 22.4 / 1 / 273)) / (273 + 20) = 0.000208 \text{ g-mole/liter}$$

$$[He-3]_0 = 0 \text{ g-mole/liter}$$

$$[NT_3]_0 = 0 \text{ g-mole/liter}$$

and the rate of ammonia formation at time zero is, using Equation 6:

$$\begin{aligned} \text{Rate}_0 &= k_1 * [T_2]_0^3 * [N_2]_0 - k_2 * [NT_3]_0^2 \\ &= 1.462 * 0.103781^3 * 0.000208 - 0.09 * 0^2 \\ &= 3.40E-7 \text{ g-mole/liter/hr} \end{aligned}$$

At time $t=t_1=t_0+\Delta t$, Δt is a small increment of time, the ammonia formed is

$$\Delta[NT_3]_1 = \text{Rate}_0 * \Delta t = 3.4E-7 * \Delta t \text{ g-mole/liter},$$

the concentrations of the gases are

$$[T_2]_1 = [T_2]_0 - \Delta[NT_3]_1 * 3/2 - [He-3]_1 / 2 \text{ g-mole/liter}$$

$$[N_2]_1 = [N_2]_0 - \Delta[NT_3]_1 * 1/2 \text{ g-mole/liter}$$

$$[He-3]_1 = 2 * [T_2]_0 * (1 - \exp(-0.00000643 * t)) \text{ g-mole/liter}$$

$$[NT_3]_1 = [NT_3]_0 + \Delta[NT_3]_1 \text{ g-mole/liter}$$

and the rate of ammonia formation is

$$\text{Rate}_1 = k_1 * [T_2]_1^3 * [N_2]_1 - k_2 * [NT_3]_1^2$$

The steps are repeated to calculate the concentration of NT₃ as a function of time. The results are plotted in Figure 6. This figure shows that the formation of ammonia is very slow. It takes about 860 hours (35 days) to convert half of the nitrogen to tritiated ammonia, and much more than 1000 hours (40 days) to reach equilibrium.

The maximum concentration of ammonia is reached when the reaction arrives at equilibrium. At equilibrium, Equation 6 equals zero:

$$\text{Rate} = k_1 * [T_2]^3 * [N_2] - k_2 * [NT_3]^2 = 0$$

$$\text{or } [NT_3]^2 / ([T_2]^3 [N_2]) = k_1 / k_2 = 1.462 / 0.09 = 16.2 \quad (7)$$

Since

$$[T_2] = [T_2]_0 - [NT_3] * 3/2 \quad (\text{Tritium decay neglected})$$

$$\text{and } [N_2] = [N_2]_0 - [NT_3] * 1/2$$

Substituting the above into equation (7):

$$[NT_3]^2 / ([T_2]_0 - [NT_3])^3 / ([N_2]_0 - [NT_3]) = 16.2 \quad (8)$$

Solving Equation 8 above will give the maximum concentration of NT_3 .

Equation 8 is a quartic equation and is better solved by trial-and-error, since we know that the maximum of NT_3 must be within 0 to $2*[N_2]_0$ (0 to 0.000416 g-mole/liter). We find that when NT_3 is 0.000398 g-mole/liter, the left side of Equation 8 equals 16.2 the same as the value of K. Therefore the maximum NT_3 concentration is 0.000398 g-mole/liter. At that point 96% of the nitrogen will have been converted to NT_3 . It takes much more than 40 days ($=1,000/24$) to reach this equilibrium.

(2) The second case involves the release of 10 g of tritium into a 600 ft³ nitrogen atmosphere glovebox.

Given:

Glovebox volume:	600 ft ³
Total pressure:	1 atm
Gas temperature:	20 °C
Initial tritium quantity:	10 g

Calculate:

Tritiated ammonia NT_3 as a function of time.
The maximum NT_3 that can be produced.

Solution:

At time zero,

the concentrations of tritium and nitrogen in terms of g-mole/liter are:

$$[T_2]_0 = 10/6 / (600 * 28.32) = 9.81E-5 \text{ g-mole/liter}$$

$$[N_2]_0 = 1 * 1 / (1 * 22.4 / 273) / (273 + 20) - 9.81E-5 = 0.041 \text{ g-mole/liter}$$

$$[He-3]_0 = 0 \text{ g-mole/liter}$$

$$[NT_3]_0 = 0 \text{ g-mole/liter}$$

and the rate of ammonia formation at time zero is, using equation (5):

$$\begin{aligned} \text{Rate}_0 &= k_1 * [T_2]_0^3 * [N_2]_0 - k_2 * [NT_3]_0^2 \\ &= 1.462 * 9.81E-5^3 * 0.041 - 0.09 * 0^2 \end{aligned}$$

$$=5.66\text{E-}14 \text{ g-mole/liter/hr}$$

Using the same method as above to calculate the amount of NT₃ as a function of time. The results are plotted in Figure 7. In comparison with the mix tank case, the formation of NT₃ is 7 orders of magnitude slower in the glovebox case. It takes about 100 hours to produce 5.7E-12 g-mole/liter of NT₃, which is 9.7E-8 g-mole in the 600 ft³ glovebox (5.7E-12*28.32*600).

At equilibrium, the NT₃ concentration is 7.8E-7 g-mol/liter, or 7.8E-7*3/2/9.81E-5=1.19% of the T₂ is converted to NT₃.

The Effect of T₂ Concentration

Equations 6 and 7 indicate that the concentration of T₂ has the strongest effect on both the NT₃ formation rate and the maximum concentration of NT₃ at equilibrium. To illustrate the magnitude of this effect, a mixture of T₂ and N₂ at 1 atm total pressure, and 20 °C temperature can be considered. When the T₂ concentration increases from 0 to 100%, the rate of NT₃ formation increases from zero, through a maximum of 4E-7 g-mol/liter/hr, then back to zero. The maximum rate occurs when the tritium concentration is about 70%. See Figure 8.

An increase in total pressure increases the concentration which increases the rate. When the total pressure is increased from 1 atm to 3 atm, the maximum rate increase by two orders of magnitude, to about 3E-5 g-mol/liter/hr. See Figure 8.

The effect of tritium concentration on the equilibrium concentration of NT₃ and the maximum amount of T₂ converted to NT₃ is shown in Figure 9. This figure shows that, at 1 atm total pressure, the equilibrium concentration of NT₃ attains a maximum of 0.0018 g-mole/liter at a T₂ fraction of 0.7. The maximum conversion of T₂ is 0.1 fraction at a T₂ fraction of 0.4.

The maximum conversion of T₂ for several particular cases of interest are given in Table 2.

Comparisons To The Walters Model

In reference 2, Walters proposed the following rate law for the formation of NT₃ from T₂ and N₂:

$$\text{Rate} = \frac{d[\text{NT}_3]}{dt} = \frac{2 * k_1 * \emptyset * 57.8 * [\text{N}_2] * [\text{T}_2]^2}{1 + \emptyset * [\text{T}_2]} \quad (9)$$

where $k_1=4.23\text{E-}6$, and $\emptyset=58.14$.

As described in reference 2, equation (9) was analytically integrated to yield an approximation to show the NT₃ concentration as a function of time:

$$[NT_3] = \frac{2 \cdot A \cdot B [1 - \exp(-kt)]}{3 \cdot B - A [\exp(-kt)]} \quad (10)$$

where, $A=[T_2]_0$, $B=[N_2]_0$, $k=3.56E-5$.

Equation 10 does not fit the data given in Table 1. The calculated concentration of NT₃ is much smaller than the data. When the value of k is multiplied by a factor of 10, Equation 8 fits the early part of the data up to about 200 hours. After that the calculated value becomes much higher than the data. Another difficulty with equations 9 and 10 is that the decomposition of NT₃ has not been taken into account. The equations do not predict an equilibrium and the reaction will go to completion, contrary to the experimental data. The data show that there is an equilibrium, when only about 23% of the tritium is converted to NT₃. Walters' model, the model of this work and the data are compared in Figure 10.

Comparisons To The Maienschein Model

In reference 1, Maienschein of LLNL considered the release of tritium into a nitrogen glovebox and proposed the following rate equation:

$$NT_3 \text{ rate} = 3.54E-12 \cdot M \quad \text{mole/sec} \quad (11)$$

where M is curies of tritium in a volume V . The equation was developed by assuming that all the β particles are absorbed by the nitrogen and that the G factor for NT₃ formation is 1. The G factor is defined as the number of molecules produced per 100 eV of energy absorbed. This equation shows that the rate is dependent on the tritium concentration alone, and is independent of N_2 and NT₃ concentrations.

To compare with the rate equation of this work, we let $V=1$ liter and change the units:

$$\begin{aligned} M (\text{curies/liter}) &= [T_2] (\text{moles/liter}) \cdot 6 \cdot 9600 \\ 1 \text{ hour} &= 3600 \text{ seconds.} \end{aligned}$$

Equation (11) becomes

$$\begin{aligned} [NT_3] \text{ rate} &= 3.54E-12 \cdot 6 \cdot 9600 \cdot 3600 \cdot [T_2] \\ &= 7.34E-4 \cdot [T_2] \quad \text{mole/liter/hr} \end{aligned} \quad (12)$$

The NT₃ formation rates for 3 cases are calculated with Equation 12 and Equation 6 respectively, and are compared in Table 3.

Table 3 shows that the Maienschein model overestimates the rates for cases that involve both low and high tritium concentrations. This is consistent with his assumptions. He assumed that all the β particles are absorbed by the nitrogen atoms and that the G factor for NT₃ formation is 1. These assumptions are most likely to be met when the ratio of T₂ to N₂ is about 1. When the ratio is much smaller or larger than 1, it is most likely that only a fraction of the β particles are absorbed by the nitrogen, or only a fraction of those absorbed can form NT₃.

On the percentage of tritium that can be converted to NT₃ in a nitrogen glovebox situation, Maier schein estimated a minimum of 10 % T₂ will be converted to NT₃ in about 80 hours. This work shows that the final conversion is dependent on the concentrations of T₂ and N₂. The maximum conversion of tritium is about 10% which occurs when the initial ratio of T₂ and N₂ is about 0.4 (see Figure 9). Equilibrium takes weeks and months, dependent on the T₂ concentration (see Figures 6 and 7).

The Effect of Oxygen and Other Gases

The reaction between T₂ and O₂ at high tritium concentrations was studied by Dorfman, and a first order rate equation was established:⁴

$$R=k*[T_2] \quad (13)$$

where

$$k=1.2E-4 \text{ /min} = 7.2E-3/\text{hr}$$

$$[T_2]=\text{tritium concentration}$$

In the case of a mix tank of tritium at 2.5 atm and 20°C, containing a small amount of oxygen and nitrogen, the tritium concentration is 0.1 g-mol/liter (see Table 2). The rate of converting T₂ to T₂O is calculated by equation 13:

$$7.2E-3 \times 0.1 = \text{to be } 7.2E-4 \text{ g-mol/liter/hr,}$$

which is much faster than the NT₃ formation rate of 3.4E-7 g-mole/liter/hr (see Table 2). Therefore in the presence of both O₂ and N₂, T₂O will form before NT₃.

At low tritium concentrations, Casaletto et al found a second order reaction rate equation:⁴

$$R=k*[T_2]^2 \quad (14)$$

where

$$k=6.2E-4 \text{ ml/mCi/hr} = 35.7 \text{ g-mole/liter/hr}$$

$$(1 \text{ mCi/ml} = 1.736E-5 \text{ g-mole/liter})$$

$$(1 \text{ g-mole/liter} = 57600 \text{ mCi/ml})$$

For 10 g T₂ released to a 600 ft³ nitrogen glovebox, the T₂ concentration is 9.8E-5 g-mole/liter. From equation 12, the T₂O formation rate is

$$35.7 \cdot (9.8\text{E-}5)^2 = 3.4\text{E-}7 \text{ g-mole/liter/hr}$$

which is again much larger than the NT₃ formation rate of 5.7E-14 g-mole/liter/hr (see Table 2). Therefore at low tritium concentration, T₂O forms before NT₃ also.

When there are other gases other than T₂, O₂ and N₂ present, such as He, D₂ and H₂, there should at least be a dilution effect, which would lower the NT₃ formation rate. Therefore the rate equation presented in this work should define the upper bound for these mixtures. More data will be required to define the quantitative effects of these other gases.

References

1. Jon L. Maienschein, "Radiolysis in Nitrogen-Tritium Mixtures: Formation of Ammonia in a Nitrogen-Atmosphere Glovebox", UCRL-90645, 4/84.
2. R. T. Walters, "Ammonia Formation in Nitrogen-Tritium Systems" DPST-85-553, 6/30/85.
3. R. T. Walters, "Kinetics and Mechanism for the Radiolytic Formation of NT₃" WSRC-TR-91-390, 5/29/91.
4. G. J. Casaletto, L. H. Gevantman and J. B. Nash, "The Self-Radiation Oxidation of Tritium in Oxygen and Air", USNRDL-TR-565, Naval Radiol. Def. Lab., San Francisco, CA, 1962.

Table 1 Experimental Data of Tritiated Ammonia Formation (Reference 3)**Tritiated Ammonia Formation Data**

(Data from R. T Waters, WSRC-TR-91-390, 5/29/91)

Total pressure at time zero = 2218 torr

Total volume = 1.456 Liter

[T₂]_o = 0.061 g-mol/L[N₂]_o = 0.062 g-mol/L

Time hr	P torr	T °C	[NT ₃] g-mol/L	Time hr	P torr	T °C	[NT ₃] g-mol/L
0	2218	16.8	0	642.70	2069	15.6	0.0080
19.00	2190	14.3	0.0005	650.10	2080	17.3	0.0081
25.42	2220	18.4	0.0006	666.72	2080	17.7	0.0083
90.92	2168	15.2	0.0021	674.33	2094	19.7	0.0083
98.00	2173	16.1	0.0022	691.92	2080	18.8	0.0087
114.92	2158	15.0	0.0026	698.22	2073	17.2	0.0085
122.00	2162	15.9	0.0028	762.97	2092	20.6	0.0088
188.75	2151	16.8	0.0038	770.33	2054	15.2	0.0087
193.83	2172	19.6	0.0038	786.70	2057	15.4	0.0087
255.12	2152	18.9	0.0046	794.17	2054	15.1	0.0087
260.35	2122	15.0	0.0047	810.75	2055	15.4	0.0088
284.47	2118	15.0	0.0049	818.20	2056	15.7	0.0088
289.95	2143	18.4	0.0049	835.27	2049	14.8	0.0089
306.80	2115	15.1	0.0051	842.08	2050	14.9	0.0089
313.50	2127	16.8	0.0052	858.78	2041	13.7	0.0089
355.32	2107	15.1	0.0056	866.37	2066	17.0	0.0088
362.20	2116	16.4	0.0056	930.38	2043	14.5	0.0091
428.50	2092	14.3	0.0061	938.37	2063	17.3	0.0091
433.82	2118	18.0	0.0062	955.03	2061	17.0	0.0091
451.78	2089	14.4	0.0063	961.83	2053	16.0	0.0092
457.88	2116	18.1	0.0063	978.83	2056	16.5	0.0092
474.85	2091	15.1	0.0065	1006.82	2084	20.1	0.0091
481.97	2100	16.8	0.0067				
498.83	2087	15.4	0.0069				
506.12	2104	19.4	0.0075				
522.65	2066	15.0	0.0079				
530.23	2077	16.5	0.0079				
594.70	2067	14.8	0.0078				
602.33	2076	15.9	0.0077				
618.78	2071	15.6	0.0079				
625.92	2084	17.3	0.0079				

Table 2 Effect of Concentration on Maximum Conversion

	[T ₂] (g-mole/liter)	[N ₂] (g-mole/liter)	Maximum conversion (%T ₂ converted)
10 ⁻² μ Ci/cc T ₂ in N ₂ glovebox	1.74E-10	0.041	1.6E-05
0.2% N ₂ in T ₂ at 2.5 atm	0.103781	0.000208	0.58% (95.7% N ₂)
10 g T ₂ in 600 ft ³ N ₂ (1 atm)	9.81E-5	0.041	1.2
177 g T ₂ in 600 ft ³ N ₂ (1 atm)	0.017	0.024	10.2
Experimental case (total P=2218 torr)	0.06	0.06	23.3

Table 3 Comparison of the Rate Equations

	[NT ₃] rate (g-mol/liter/hr)	
	This Work Eq. 6 G factor= $f([T_2], [N_2], [NT_3])$	Maienschein Eq. 12 G factor=1
(1) 10-2 μ Ci/cc T ₂ in N ₂ glovebox	3.2E-31	12.8*E-14
(2) 10 g T ₂ in 600 ft ³ N ₂ glovebox [T ₂]=9.8E-5 g-mol/liter [N ₂]=0.0415 g-mol/liter	5.7E-14	71.9E-9
(3) 2218 torr total pressure (data case) [T ₂]=0.06 g-mol/liter [N ₂]=0.06 g-mol/liter	1.9E-5	4.4E-5
(4) 99.8 mol% T ₂ , 0.2 mol% N ₂ , 2.5 atm [T ₂]=0.103 g-mol/liter [N ₂]=0.00021 g-mol/liter	3.4E-7	7.6E-5

Figure 1 Tritiated Ammonia Formation Experimental Data

Figure 2. Rate Data Calculated From The Experimental Data

To Find The Constants

Figure 3. The Rate Equation Constants

Figure 4. Rate Data vs. The Rate Equation

Experimental Data vs Calculation

Figure 5 Tritiated Ammonia Formation Data vs. Calculation With The Rate Equation

Ammonia Formation In A Mix Tank

Figure 6. Tritiated Ammonia Formation in A Mix Tank

Ammonia Formation In A Nitrogen Glovebox

Figure 7. Tritiated Ammonia Formation in A Nitrogen Glovebox

Concentration Effect on NT3 Formation Rate

Figure 8. T₂ Concentration Effect on Tritiated Ammonia Formation Rate

Tritium Concentration Effect On Maximum Conversion

Figure 9. T₂ Concentration Effect on Equilibrium NT₃ Concentration and T₂ Conversion

Experimental Data vs Calculation

Figure 10. Current Model vs. Walters Model

Appendix 1 Derivation of The Equation For Calculating NT₃ Concentration From Experimental Data of Pressure, Temperature and Time.

The reaction equation is

Ideal gas law: $P \cdot V = n \cdot R \cdot T$

where P: pressure
V: volume
n: number of moles
R: gas constant
T: Temperature.

At time=0

Tritium partial pressure $P_{\text{Tr}} = P_{\text{Tr}_0}$

Nitrogen partial pressure $P_{\text{N}} = P_{\text{N}_0}$

Tritiated Ammonia partial pressure $P_{\text{A}} = P_{\text{A}_0} = 0$

Total pressure $P = P_0 = P_{\text{Tr}_0} + P_{\text{N}_0} + 0$

and the concentrations are, in g-mole/liter:

$$[\text{T}_2]_0 = P_{\text{Tr}_0} / (R \cdot T_0)$$

$$[\text{N}_2]_0 = P_{\text{N}_0} / (R \cdot T_0)$$

$$[\text{NT}_3]_0 = P_{\text{A}_0} / (R \cdot T_0) = 0$$

$$\text{total moles} = [\text{T}_2]_0 + [\text{N}_2]_0 = P_0 / (R T_0)$$

At time=t

$$[\text{NT}_3]_t = P_{\text{A}_t} / (R \cdot T_t)$$

$$[\text{He-3}]_t = 2 \cdot [\text{T}_2]_0 \cdot [1 - \exp(-\lambda \cdot t)] \quad (\lambda = \text{T}_2 \text{ decay constant} = 6.43\text{E-6 hr}^{-1})$$

$$[\text{T}_2]_t = [\text{T}_2]_0 - [\text{NT}_3]_t \cdot (3/2) - [\text{He-3}]_t \cdot (1/2)$$

$$= [\text{T}_2]_0 - [\text{NT}_3]_t \cdot (3/2) - [\text{T}_2]_0 \cdot [1 - \exp(-\lambda \cdot t)]$$

$$[\text{N}_2]_t = [\text{N}_2]_0 - [\text{NT}_3]_t \cdot (1/2)$$

$$\text{total moles} = P_t / (R T_t)$$

$$= [\text{NT}_3]_t + [\text{He-3}]_t + [\text{T}_2]_t + [\text{N}_2]_t$$

$$= [\text{NT}_3]_t$$

$$+ 2 \cdot [\text{T}_2]_0 \cdot [1 - \exp(-\lambda \cdot t)]$$

$$+ [\text{T}_2]_0 - [\text{NT}_3]_t \cdot (3/2) - [\text{T}_2]_0 \cdot [1 - \exp(-\lambda \cdot t)]$$

$$+ [\text{N}_2]_0 - [\text{NT}_3]_t \cdot (1/2)$$

Rearranging to give the final form of the equation:

$$[\text{NT}_3]_t = P_t / (R T_t) + [\text{T}_2]_0 + [\text{N}_2]_0 + [\text{T}_2]_0 \cdot [1 - \exp(-\lambda \cdot t)]$$

$$= - P_t / (R T_t) + P_0 / (R T_0) + P_{\text{Tr}_0} / (R \cdot T_0) \cdot [1 - \exp(-\lambda \cdot t)]$$

$$= (1/R) \cdot [- P_t / T_t + P_0 / T_0 + (P_{\text{Tr}_0} / T_0) \cdot [1 - \exp(-\lambda \cdot t)]]$$

DISTRIBUTION:

J. R. Knight, 773-A
T. Motyka, 773-A
J. R. Dollar, 232-H
A. F. Reichman, 773-A
M. W. Lee, 773-A
A. S. Horen, 773-A
J. E. Klein, 773-A
J. H. Scogin, 773-A
D. L. Hayes, 235-H
D. J. Green, 235-H
R. A. Pedde, 235-H
R. D. Buley, 235-H
T. R. Davis, 235-H
D. U. Randolph, 233-5H
W. B. Wilson, 703-42A
TIM Office, 703-43A (4 copies)

DATE

FILMED

6 / 2 / 94

END

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

1