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NERVA IRRADIATION PROGRAM

GTR Test 21

Volume 2

Nuclear-Radiation-Induced Conversion of Parahydrogen to Orthohydrogen

NUCLEAR AEROSPACE RESEARCH FACILITY

operated by

GENERAL DYNAMICS

Fort Worth Division

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NUCLEAR AEROSPACE RESEARCH FACILITY

NERVA IRRADIATION PROGRAM
GTR Test 21
Volume 2

**Nuclear-Radiation-Induced Conversion
of Parahydrogen to Orthohydrogen**

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Space Nuclear Propulsion Office
of the
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Cleveland, Ohio 44135

Contract No. AF 29(601)-7077
Supplement 10

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FOREWORD

The work described in this document was performed at the Nuclear Aerospace Research Facility (NARF) of the Fort Worth Division of General Dynamics for the Space Nuclear Propulsion Office, Cleveland, Ohio (SNPO-C) under Statement of Work No. 4 (Attachment H), Contract AF29(601)-7077, Supplemental Agreement No. 10.

The conversion of parahydrogen to orthohydrogen as a result of nuclear irradiation was investigated as a part of GTR Test 21, which is the most recent of a series of tests being conducted on NERVA components and materials for SNPO-C. The other parts of GTR-21 are reported in Volumes 1, 3, and 4 of FZK-351. These reports concern, respectively, the evaluation of a hydrogen-gas detector, the thermal conductivity and resistivity of materials, and materials structural properties.

The valuable assistance given by D. H. Weitzel of the National Bureau of Standards, Boulder, Colorado, is gratefully acknowledged. Acknowledgment is also given to J. W. Guinn for the electronic design of the para-orthohydrogen analyzer and to D. J. LaJaunie for the analyzer construction.

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SUMMARY

This report describes an experiment designed to investigate the conversion of parahydrogen to orthohydrogen by nuclear radiation.

A model for conversion is postulated that assumes that certain products formed in liquid parahydrogen during irradiation ultimately cause conversion in the gas. The model is based on data from an exploratory analysis of the hydrogen gas issuing from a materials test dewar during a NARF irradiation; related experimental work such as that of Blue and Fessler and Zessoules, et al; nuclear energy absorption processes in hydrogen; and general $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ conversion principles. To test the model, samples of liquid parahydrogen (up to 15 gal/sample) were irradiated by the Ground Test Reactor (GTR).

A double-vessel dewar in which the sample hydrogen contained in the inner vessel could be totally immersed in LH_2 contained in the outer vessel was constructed for the irradiation. Gas was continuously bled from the active-volume effluent during irradiation and piped to a para-orthohydrogen analyzer located some 70 ft away for analysis.

Measurement of the orthohydrogen content of the effluent was by means of a continuous flow gas analyzer of the thermal-conductivity type. It was also constructed especially for the

test and has an accuracy of 0.3% parahydrogen.

Irradiation data were obtained covering a gamma range of from 1.7×10^8 to 1.2×10^9 ergs/g(C)-h and a neutron range of from 2.2×10^{14} to 1.6×10^{15} n/cm²-h ($E > 1.0$ MeV). Large amounts of conversion were observed, the highest reported being reduction of 99% p-H₂ to 38% p-H₂ ($\approx 49\%$ relative conversion). The conversion was unmistakably due to nuclear radiation.

Two experimental runs, selected because of their widely differing conditions, were chosen for comparison with calculations. A quantitative description of the model was formulated, and calculations were made of the conversion of parahydrogen to orthohydrogen for the conditions of the two runs considered. Order-of-magnitude agreement was obtained between the calculations and the experimental data, and agreement between the calculated and observed effects of both boiloff rate and reactor power was also reasonably good. On the basis of the overall conformity of the theoretical results with the experimental data, it is tentatively concluded that the model is essentially correct.

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I. INTRODUCTION

Propellant for the NERVA engine is stored as liquid parahydrogen in a reservoir attached to the engine. During an engine run the hydrogen is pumped from the reservoir, through a cooling jacket on the nozzle skirt, past the reflector, through the shield, into the hot reactor core, and then through the nozzle. The process involves exposure of the propellant to nuclear radiation.

In addition to the primary function as a propellant, the hydrogen serves as a reactor coolant. Since the thermal properties of hydrogen vary with the para-to-orthohydrogen ratio, any possible effects of nuclear radiation on this relationship become of extreme interest.

An exploratory analysis of the hydrogen effluent from the NARF experiment (Ref. 1) produced a positive indication of conversion. Although the possibility of such a phenomenon had been postulated earlier by Corruccini (Ref. 2) and others, this was the first known experimental demonstration of the conversion of parahydrogen to orthohydrogen by nuclear radiation. A sample stream bled from hydrogen gas issuing from a dewar in which electronic components were being tested in a combined LH_2 -nuclear radiation environment was monitored with a continuous-flow para-orthohydrogen gas analyzer for changes

in para-ortho composition. The amount of conversion was small (1/2 to 3 p-H₂%), but was sufficient to excite further interest since the mechanism suggested by the experiment implied that under propitious conditions much more extensive conversion could be expected.

The experiment described in this report evolved directly from the exploratory analysis and had the primary purpose of determining if radiation from a nuclear reactor can cause significant para-to-orthohydrogen conversion. Secondary objectives were to establish a quantitative relationship between radiation intensity and conversion and to gain further insight into what any radiation-induced conversion mechanism might be. The experiment was based on the following hypothesis:

Radiation products capable of causing para-to-ortho conversion are introduced into liquid hydrogen through interaction of the impinging radiation with the liquid itself, objects immersed therein, and the walls of the containing vessel. These species are relatively stable in the liquid and their concentration in the liquid builds up with irradiation time to a level principally determined by the stability of the products in the liquid, the radiation intensity, the probability for formation, and the boiloff rate. The species probably do not cause significant para-to-ortho conversion in the liquid because the lowest ortho energy level is almost vacant at LH₂ temperatures.

The radiation products evaporate from the liquid along with the other liquid constituents. The higher prevailing temperatures associated with the gas phase permit the products to cause parahydrogen to convert to orthohydrogen but,

at the same time, the increase in temperature reduces the stability of the products. The degree of conversion is limited principally by the para-to-ortho equilibrium ratio for the temperature of the reaction site, the concentration of radiation products at the reaction site, and the reaction rate applicable to the temperature of the reaction site.

The test itself was conducted by irradiating liquid parahydrogen with gamma rays and neutrons from a nuclear reactor. Gas evolved from the liquid undergoing irradiation was bled from the ullage space of the irradiation vessel and piped to a flow-type para-orthohydrogen gas analyzer where it was continuously analyzed (including irradiation periods) for orthohydrogen content.

The results, which cover the gamma-dose-rate range of $1.7 - 12 \times 10^8$ ergs/g(C)-h and the concomitant neutron flux range of $2.2 - 16 \times 10^{14}$ n/cm²-h ($E > 1.0$ MeV), are in general agreement with the hypothesis. Up to 62% orthohydrogen content was measured ($\approx 49\%$ relative conversion).

A quantitative description of the qualitative model was formulated and calculations were made of the conversion of parahydrogen to orthohydrogen for the conditions of two of the experimental runs so selected as to embody discriminating histories. To make these calculations, parameters for the rates of production and vaporization of the H-atom parent (an H₃ complex) were obtained from an independent calorimetric

experiment. The quantity of H atoms surviving to the warm region was calculated (a) by assuming homogeneous recombination with H_2 molecules serving as the third bodies, and (b) by using a three-body recombination coefficient estimated from application of steric factors to data on dissociation of hydrogen at elevated temperatures.

Finally, the amount of exchange conversion induced by the H atoms that survived recombination long enough to reach the warm region where conversion is possible was calculated using a published rate constant for H- H_2 exchange. On the basis of the overall conformity of the theoretical results with the experimental data, it is tentatively concluded that the model is essentially correct.

II. DISCUSSION OF PARA-TO-ORTHOHYDROGEN CONVERSION

2.1 Radiation-Produced Species in Hydrogen

Energy deposited in a hydrogen absorber by nuclear radiation is initially transferred to scattered electrons, in the case of gamma radiation, or to recoil protons, in the case of neutron radiation.

As these charged particles pass through the absorber, approximately equal amounts of energy go into the production of H-atom pairs and H_2 ions. The H atoms and H_2 ions in turn cause further dissociation and ionization. It has been estimated that about 43% of the deposited energy is temporarily stored in the production of such species (Ref. 3). The remainder is given up almost immediately as heat.

What the lifetime of these radiation-produced species might be is a subject of considerable interest.

Zessoules, Brinkerhoff, and Thomas measured the mobilities and recombination coefficients of species produced by neutron irradiation of a liquid-hydrogen flow system and concluded that recombination was virtually instantaneous except for a small fraction of about 1.7×10^{-4} of the volumetric ionization rate (Ref. 4). However, the data only permit estimation of H_2^+ and H_2^- concentration in the liquid, and cast no light upon the H-atom situation.

Blue and Fessler used a vapor-pressure method to measure the ortho-to-parahydrogen conversion caused by fast-neutron irradiation of liquid normal* hydrogen (Ref. 5). The conclusion was that conversion was caused by an atomic or molecular species which appeared to have a long-lived (~ 5 min) precursor. It was further concluded that the precursor was not one of the primary radiation products (H_2^+ or e^-).

2.2 Conversion Not Likely in Liquid Phase

The conversion observed in the exploratory experiment at NARF was associated with the liquid (Ref. 1). Although observed to be associated with the liquid this is not to suggest that conversion actually occurred there, but rather that the process which ultimately led to conversion seemed to be largely initiated there.

It should be emphasized that though the Blue and Fessler experiment observed conversion in the liquid, the conversion was from orthohydrogen to parahydrogen. Orthohydrogen is a non-equilibrium state at LH_2 temperatures; hence any catalyst, radiation-induced or otherwise, will promote conversion from the ortho to the para modification. The reverse, however, is not true as liquid parahydrogen is already in the equilibrium state. Therefore, the only credible means for radiation to

*Hydrogen composed of 25% para- and 75% orthohydrogen - the ratio obtained at room temperature.

induce $p\text{-H}_2 \rightarrow o\text{-H}_2$ conversion in the liquid is for the radiation to induce dissociation of the $p\text{-H}_2$ molecule so that the freed atoms might recombine as orthohydrogen.

Although it is unlikely that all such interactions would lead directly to the formation of orthohydrogen, a consideration of data from the exploratory experiment shows that even on the basis of 100% efficiency, and with no reconversion, not enough energy was absorbed to obtain the 3% conversion observed.

For example, the gamma dose rate was 2×10^9 ergs/g(C)-h (the neutron dose rate was negligible in comparison), which corresponds to a dose rate in H_2 of $2 \times 10^9 \times 0.055/0.028 = 4 \times 10^9$ ergs/g(H_2)-h, where 0.055 and 0.028 are the mass-absorption coefficients for energy absorption in hydrogen and carbon, respectively. The molecular weight of H_2 is 2.016, and the conversion factor from eV to ergs is 1.6×10^{-12} ; therefore, the energy absorption rate for 1 mole was very nearly $2 (4 \times 10^9)/1.6 \times 10^{-12} = 5 \times 10^{21}$ eV/h-mole. The average irradiation time was about 1/3 h; hence the dose rate per mole was about $(1/3) 5 \times 10^{21} = 1.7 \times 10^{21}$ eV/h mole. About 36 eV are lost by the primary radiation products in each collision, so the maximum number of o-H molecules formable by a strict dissociation-recombination sequence was no greater than $1.7 \times 10^{21}/36 = 4.7 \times 10^{19}$ o-H molecules/mole. This corresponds to a concentration of about 0.008%, which is more than three orders

of magnitude less than the 3% observed. Obviously then, a more complex process than simple dissociation-recombination was involved. In the following subsection a mechanism is suggested wherein nuclear radiation might cause extensive conversion of parahydrogen to orthohydrogen.

2.3 Proposed Model for Radiation-Induced Conversion

Species capable of causing $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ conversion are introduced into liquid parahydrogen by the impinging radiation. These species are virtually stable in the liquid and their concentration therefore builds up with irradiation time to a level principally determined by the radiation intensity, the cross-section for formation, and the evaporation rate. Little or no conversion is initiated by the species while they are in the liquid because the hydrogen molecules with which the species can interact are already at the equilibrium para-ortho composition.

The species evaporate in proportion to their concentration in the liquid. Higher temperatures are associated with the evolved gas, so the H_2 is no longer necessarily at the equilibrium para-ortho composition. Once in the gas, therefore, the species interactions with H_2 molecules can initiate (cause) $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ conversion, possibly by paramagnetic catalysis or three-body recombination. The amount of conversion obtainable in this manner is a function not only of specie concentration, but also a function of the equilibrium $o\text{-H}_2/p\text{-H}_2$ ratio and the

efficacy of the $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ reaction. Both of the latter increase with temperature.

In contrast to their virtual stability when in the liquid the species are unstable in the gas and die rapidly, the death rate increasing with temperature. Thus, an increase of gas temperature has three principal effects:

1. The equilibrium orthohydrogen fraction is increased.
2. The efficacy of the species in causing the $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ reaction is increased.
3. The death rate of the species is increased.

Any given real system for irradiation of liquid hydrogen can be arbitrarily subdivided into three major regions of interest: the liquid, the cold-gas, and the warm-gas regions. The role of each in light of the foregoing qualitative model is summarized below:

- Liquid Region

- Species capable of causing $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ conversion are created by interaction of impinging radiation.
- The species are stable and concentration builds up with radiation time to a saturated value.
- No conversion is caused because the H_2 is at para-ortho equilibrium.

- Cold-Gas Region

- Species are unstable and die rapidly.
- Little conversion is caused because of the ceiling imposed by the low orthohydrogen equilibrium value

associated with the low temperature.

- Residence time, death rate, and temperature determine the quantity of species that survive.
- Warm-Gas Region
 - The species cause $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ conversion in this region.
 - The degree of conversion is a function of the concentration of species, the reaction rate, and reaction time.

Later (Section V) it will be shown that for a three-region model such as above, the quantitative relationships exhibited below without proof hold for the case of constant liquid replenishment.

The fractional conversion to normal hydrogen is given by the expression

$$P(\theta) \approx 1 - e^{-k[H]_{co}\theta} \quad (2-1)$$

where

$P(\theta)$ = fractional conversion to normal hydrogen

k = rate constant for $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ conversion at temperature T

$[H]_{co}$ = concentration of H atoms entering the warm gas region

θ = time in warm-gas region

The quantity $[H]_{co}$ is in turn given by the expression

$$[H]_{co} = \frac{[H]_{uo}}{1 + 2 R_u [H_2]_u [H]_{uo} t} \quad (2-2)$$

where

$[H]_{uo}$ = H-atom concentration immediately over the liquid surface

R_u = recombination coefficient in the cold-gas region for H-atom pairs with H_2 as the third body

t' = time in cold gas region

Finally, $[H]_{uo}$ in Equation 2-2 is given by the expression

$$[H]_{uo} = \frac{P_r}{\dot{\beta}} \frac{\rho_g}{\rho_l} (1 - e^{-f\dot{\beta}t}) \quad (2-3)$$

where

P_r = production rate of species in LH_2 (by radiation)

$\dot{\beta}$ = fractional boiloff rate

ρ_g = density of cold gas region

ρ_l = density of liquid

f = fugacity of radiation-produced species

t = radiation time

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III. TEST SETUP AND PROCEDURE

The radiation source for the experiment was the NARF Ground Test Reactor (GTR), which has a maximum power generation of 10 MW (thermal). A gamma dose rate as high as 2.4×10^9 ergs/g(C)-MW-h and a neutron flux as high as 1.6×10^{15} n/cm²-MW-h ($E > 1.0$ MeV) are available at the primary irradiation positions. A brief description of the GTR Radiation Effects Testing System is given in Appendix C.

3.1 Test Setup

The flow diagram in Figure 3-1 indicates the interrelationship of the major components used in the experiment. These components are described in detail in Appendix A.

Liquid parahydrogen was piped from a reservoir located outside the significant radiation field to a dewar situated adjacent to the GTR closet. A liquid-transfer control system permitted control of the fill rate and fill level so as to either maintain a constant level or merely fill the dewar to a pre-selected level. Remote control was maintained during irradiation, either automatically or manually.

After cooldown, the rate of evaporation of the LH₂ in the dewar was essentially proportional to the reactor power, since the design of the dewar was such that the thermal heat leak was negligible. To provide the capability of maintaining

Figure 3-1 Block Diagram of the Experimental System

a constant evaporation rate regardless of the reactor power, a 1000-W (maximum rating) electric heater of variable power was incorporated in the dewar design.

Samples of the gas evolved from the LH_2 were continuously bled from the dewar exhaust and routed to a flow-type gas analyzer located in the reactor control room. As shown in Figure 3-2, two lines were attached at the dewar; a third was attached to the main exhaust system at the same point used in the exploratory experiment (Ref. 1). The latter was for the purpose of checking the earlier results. The two lines attached to the dewar were of primary importance and differed only in the location of the conditioner, an enlargement in the line which could be heated to provide the high-temperature region for conversion. In the line designated Sample 1, the conditioner was located 2 ft downstream of the dewar; in the line designated Sample 2, the conditioner was 50 ft downstream.

The para-ortho composition of the sample streams was determined with a continuous-flow type gas analyzer that operates on the principle of thermal-conductivity comparison. It has an accuracy of 0.3% parahydrogen and a precision of one-tenth of that, i.e., 0.03% parahydrogen (see Appendix B for the error analysis). Three sample channels are normally available. A fluid (gas) control panel is used to select and route any of the three samples through the measurement cell (T/C cell). Bypass

Figure 3-2 Schematic of Sample-Gas Flow System

valves permit maintenance of flow through the two sample lines not being measured.

3.2 Procedure

The gas analyzer was functionally calibrated and set up in the reactor area along with the other experimental apparatus (see Appendix A). Three thermal cycles were performed with the dewar on the ramp and one with the dewar in the west irradiation position (see Appendix C) in order to qualify the apparatus as safe for irradiation. Preirradiation data was taken to calibrate the gas analyzer (see Subsection 3.3) and to verify that there was no system-caused conversion. The reactor was brought to power and the irradiation data were gathered in two sessions, approximately 12 h apart, at reactor powers of 1, 4.8, and 7.2 MW.

The parahydrogen concentration was measured under two conditions:

- As the dewar was being filled
- As the liquid level decreased after the LH_2 supply was shut off

Plans to obtain data at a constant liquid level (replenishment rate equal to evaporation rate), at constant evaporation rate, and varied evaporation rates were abandoned because the dewar heater failed.

During the course of the experiment, the reactor power

ceiling was lowered to 4.8 MW because of another experiment being run concurrently. The 7.2-MW data obtained in Session 2 (after the ceiling reduction) were acquired by using a procedure that could only be performed once without undue risk that xenon poisoning would prevent return of the reactor to power.

Table 3-1 summarizes the experimental conditions under which radiation-induced conversion data were acquired. Note that the boildown runs are not to be associated with the preceding fill run. In general, different adjustments on an outside valve were required for the fill and boildown modes; as a result, it was not possible to obtain reliable data for both the fill and boildown portions of a single cycle.

3.3 Analyzer Calibration

The preirradiation calibration, shown in Figure 3-3, was used to translate analyzer data to percent parahydrogen. The slope of the calibration line is

$$\frac{74}{19.58} = 3.78 \frac{\% \text{ parahydrogen}}{\text{mV}}$$

Data were converted to parahydrogen concentration (%) by use of the equation

$$\text{Conc.} = 99 - (R_R - R_S) 3.78$$

Table 3-1

EXPERIMENTAL CONDITIONS FOR RADIATION-INDUCED
PARAHYDROGEN CONVERSION DATA^a

Session No.	Run No.	Mode		Conditioner Temp. (°R)		Reactor Power (MW)
		Fill	Boildown	Sample 1	Sample 2	
1	1	X		496	496	7.2
1	2	X		538	538	7.2
1	3		X	538	538	7.2
1	4		X	538	538	7.2
1	5		X	538	538	7.2
2	6	X		496	496	4.8
2	7	X		496	496	4.8
2	8		X	496	496	4.8
2	9		X	845	845	4.8
2	10		X	845	845	1.0
2	11		X	845	845	7.2 & 0

^aSample line flow rate (Q) constant at 20 scfh

Figure 3-3 Analyzer Calibration Curve

where

R_R = reading of reference (source) gas (99% para, mV)

R_S = reading of sample gas (mV)

3.78 = slope of calibration curve

99 = concentration (%) of parahydrogen in the reference
gas

Since source-gas readings were frequently taken, use of the above procedure minimized any error that might result from an unnoticed zero shift, particularly at low conversion (high para concentration) levels. The parahydrogen concentration in the supply was assumed to be 99%. This assumption appears justified by the fact that a straight line passing through the two known points also passes through the assumed point.

The reference gas for the calibration and the measurements was obtained directly from the transport trailer ullage and converted, when required, to either normal hydrogen by the normalizer, or 51.5% parahydrogen (48.5% orthohydrogen) by the calibration chamber.

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IV. PRESENTATION OF RESULTS

4.1 Preirradiation Data

4.1.1 Test Hydrogen Purity

The hydrogen used for the test was of propellant grade, shipped to Fort Worth by the standard 12,000-gal transport trailer normally used for transporting liquid-hydrogen propellant. The laboratory analysis furnished by the vendor is as follows:

TEST-HYDROGEN LABORATORY ANALYSIS

Parahydrogen	>97%
Total Purity	>99.995%
Total Gaseous Impurities	<50 ppm
Selected Impurities (N ₂ , H ₂ O, Volatile Hydrocarbons)	<4 ppm
Specific Impurities	
O ₂ + A	0.08 ppm
He	<10 ppm
CO and CO ₂	<1 ppm

4.1.2 Preirradiation Run

Prior to reactor startup the dewar was filled with liquid hydrogen and measurements were made on all three sampling channels and compared with that of the reference (source) gas which was piped directly from the trailer ullage. These measurements are shown in Table 4-1. No difference was detected, showing

that in the absence of radiation the system (liquid, dewar, lines, etc.) does not cause conversion.

Table 4-1

PREIRRADIATION MEASUREMENTS OF PERCENT PARAHYDROGEN
(Conditioner Temperature = 830°R)

Source Gas (Trailer Ullage)	Sampling Channel		
	1	2	3
99.00	98.96	99.00	99.04
98.96	99.00	98.92	98.96

The slight difference in the readings is random and represents less than 0.12% parahydrogen difference between the maximum and minimum cases. Note that the high conditioner temperatures made no difference. This was even more forcefully evident during the test from actual observation of the unchanging parahydrogen readings as conditioner temperature was increased.

4.2 Irradiation Data

4.2.1 Sample History

Figure 4-1 is a schematic showing general sample history. The gamma-dose-rate and neutron-flux values were ascertained from maps of the unperturbed field and are precise to within 30%. Of this percentage, 10% is the precision of the foils and dosimeters used to obtain the maps; 5% is for uncertainty in reactor power; and the remaining 15% is to account for errors

* Residence time as liquid is a function of boiloff rate and fill level

** Residence time as ullage gas is a function of boiloff rate and liquid level

Figure 4-1 Sample History

introduced by interpolation and by the calculations of field perturbation. A relative value for nuclear parameters between two nominal reactor powers is thus within 10% ($2 \times 5\%$).

In Figure 4-1, the system components of interest are indicated by blocks; the average residence time of a particular quantity of hydrogen in a particular component is also given. The dashed lines show the pertinent regional limits of the given nuclear values; sections for which nuclear values are not given are in a nuclear field which is negligible insofar as the purposes of the test are concerned.

Sample 3 is not shown in Figure 4-1 as it was quickly apparent that there was no difference in the Sample 2 and Sample 3 data; besides, the Sample 3 line was only installed to check the results of the exploratory experiment.

4.2.2 Conversion Data

Table 4-2 summarizes the data from 11 runs, where a run is defined as a dewar filling, i.e., one dewar charge. These data are subsequently presented in more detail as time plots of measured parahydrogen concentration. In each case the plots are referenced to the run numbers given in Table 4-2, which were assigned in chronological order. Since all the "fill" data are listed in the table first, then the "boildown" data, the run numbers do not appear in numerical order.

Table 4-2

SUMMARY OF DATA

Run No.	Figure No.	Session (1 or 2)	Mode		Conditioner Temperature (°R)		Reactor Power (MW)	Approximate Boiloff Rate (gal/h)	% Para Concentration at Maximum Conversion	
			Fill	Boil-down	Sample 1	Sample 2			Sample 1	Sample 2
1	4-2	1	X		496	-	7.2	-	38	-
2	4-3	1	X		538	-	7.2	-	44	-
6	4-4	2	X		496	-	4.8	-	72	-
7	4-5	2	X		496	496	4.8	-	55	97
5	4-6	1		X	538	-	7.2	74	38	-
3	4-7	1		X	538	-	7.2	74 ^a	54	-
4	4-8	1		X	-	538	7.2	74 ^a	-	97.7
8	4-9	2		X	496	496	4.8	19	89.6	97
9	4-10	2		X	845	845	4.8	16	89.6	98
10	4-11	2		X	845	845	1.0	3 ^a	98.8	99
11	4-12	2		X	845	-	7.2	24	88.6	-
							0 (Scram)	-	98.6 ^b	

^aEstimated value^bOne minute after scram

4.2.2.1 Conversion During Dewar Fill

Figures 4-2 through 4-5 (Runs 1, 2, 6, and 7) are plots of p-H₂ concentration observed during dewar fills (with the reactor at power). In each figure, the p-H₂ concentration (percent) is plotted against time from initiation of the dewar-fill operation. The first two figures (Runs 1 and 2) show data taken during the first session; the last two figures show data taken during the second session.

In general, the fill data are characterized by high conversion (45 to 75% p-H₂ values) that is quickly achieved (note that the abscissa scale is in seconds). Another characteristic is that the high conversion level (low p-H₂ value), once achieved, runs at a rather steady value for the balance of the fill cycle.

With regard to shape, the rise portion of the data in Figure 4-4 (the portion of Run 6 after 30-35 sec) is not typical of the fill data. Usually, only 30-40 sec were required to complete the dewar-fill operation. It is believed that the fill operation had actually been completed after about 35 sec into Run 6 and that the data after this time are more indicative of the boildown condition and transition thereto. However, this cannot be established from the data tape.

In the analysis (Section V) it will be shown that the degree of conversion obtainable is heavily influenced by the time the

Figure 4-2 Parahydrogen Concentration During Dewar Fill, Run 1

Figure 4-3 Parahydrogen Concentration During Dewar Fill, Run 2

Figure 4-4 Parahydrogen Concentration During Dewar Fill, Run 6

Figure 4-5 Parahydrogen Concentration During Dewar Fill, Run 7

effluent spends in the dewar ullage space (ullage residence), which is itself governed by the boiloff rate. Because the boiloff rate during dewar fill is unknown, and probably somewhat variable, not too much significance is attached to the fact that the higher reactor power (7.2 MW as compared with 4.8 MW) produced the greater conversion in the fill mode.

Both Sample 1 and Sample 2 data were obtained during Run 7 (Fig. 4-5). The 97% p-H₂ value obtained from Sample 2 is typical of the values obtained from Sample 2 during the boildown mode. The significance of this lesser conversion (from Sample 2) is related to the ullage residence time and species attenuation problem.

Dashed lines are used to connect the datum points only as an aid in relating the points; there is no intent to convey the idea that interim points would follow the line, except in an approximate fashion. In fact, the shape of the Sample 1 data in Figure 4-5 would probably have been similar to the shape obtained in Figure 4-4 had it been possible to obtain the interim data, since in this case the data tape definitely shows that the last data point (at 28 sec) was obtained after the filling operation had been terminated. The fewer datum points, and hence indefinite shape, are a consequence of valving back and forth in order to obtain data from both samples.

4.2.2.2 Conversion During Dewar Boildown, Session 1

Figures 4-6, 4-7, and 4-8 (Runs 5, 3, and 4) show conversion data obtained during Session 1. Each of these figures is a plot showing observed parahydrogen concentration (percent) versus boildown time. Figures 4-6 and 4-7 are plots of Sample 1 data and Figure 4-8 is a plot of data from Sample 2. Be sure to note the different ordinate scale in Figure 4-8, which is expanded to 0.2% parahydrogen per 0.5-in. division, whereas the other two figures show 10% parahydrogen per 0.5-in. division. In each of these three figures, the controllable parameters, i e., reactor power and conditioner temperature, are the same, 7.2 MW and 538°R.

In Figure 4-6, the p-H₂ concentration starts at a low value (~38%), increases in about 1 min to 65%, and then slowly increases for the next 9 min to about 78%. This was the first set of boildown data recorded, and was taken when the boiloff rate was at the very high value of about 74 gal/h. The quickly achieved low p-H₂ value is typical of the Session 1 boildown data and is attributed to the considerably reduced ullage residence that results from the high boiloff rate.

The Run 3 (Fig. 4-7) data are of precisely the same type as that of Run 5 (Fig. 4-6) and are presented in the same manner. However, the shape of the curve obtained is now quite typical of that of the balance of the Sample 1 data. Notice that the

Figure 4-6 Parahydrogen Concentration During Dewar Boildown, Run 5

Figure 4-7 Parahydrogen Concentration During Dewar Boildown, Run 3

Figure 4-8 Parahydrogen Concentration During Dewar Boildown, Run 4

minimum p-H₂ value occurs at about 4 min. Once again the dashed lines used to connect the points are intended as a visual aid and only approximate the (unknown) interim values.

A measurement of the composition of the trailer ullage gas, effected by means of the plumbing modification which piped trailer ullage gas directly to the Sample 3 attachment of the analyzer, is also included in this and all subsequent figures. Since the trailer ullage gas is at the para-ortho composition of the hydrogen before irradiation, not only is the conversion obtained from irradiation emphasized, but the extreme stability of the instrument is illustrated.

Figure 4-8 shows data from Sample 2. In this case the ordinate scale has been expanded to 0.2% p-H₂ per 0.5-in. division. The extreme stability typical of data from Sample 2 is clearly evident. The p-H₂ value of slightly over 97% is also rather typical.

4.2.2.3 Conversion During Dewar Boildown, Session 2

Figures 4-9 through 4-13 show p-H₂ concentrations obtained during the dewar boildowns of Session 2. Figures 4-9 and 4-10 show data at a reactor power of 4.8 MW; Figure 4-11 shows data obtained at a reactor power of 1 MW; and Figures 4-12 and 4-13 show data obtained at a reactor power of 7.2 MW. All these figures include interspersed measurements of trailer ullage-gas composition. The last two figures are perhaps the most interesting

Figure 4-9 Parahydrogen Concentration During Dewar Boildown, Run 8

Figure 4-10 Parahydrogen Concentration During Dewar Boildown, Run 9

Figure 4-11 Parahydrogen Concentration During Dewar Boildown, Run 10

Figure 4-12 Parahydrogen Concentration During Dewar Boildown, Run 11

Figure 4-13 Parahydrogen Concentration During Dewar Boildown, Run 11: Expanded-Time Plot

of all in that they show the behavior when the reactor was scrambled from 7.2 MW in midrun.

Perhaps the most striking feature of these figures, taken as a whole, is that less conversion is evident than during Session 1, the minimum in the Sample 1 data occurring at about 89% p-H₂ level, except in the case of the 1-MW data where only very slight conversion was indicated. Conversion observed from the Sample 2 data was also less in Session 2, running at the 98% to 98%-plus p-H₂ level, although always with the small fluctuations typical of Sample 2.

As was the case with the fill data, the effect of radiation intensity is not readily apparent. Both the 4.8- and 7.2-MW reactor powers produced about the same minimum p-H₂ level (89.5% at 4.8 MW, 88.6% at 7.2 MW) from Sample 1.

Notice, too, that the minimum in the Sample 1 data typically occurs after about 4 to 6 min and, in fact, the 4.8- and 7.2-MW data are quite similar in shape as well as magnitude. The minimum in the curves is believed to be a consequence of competing effects. The concentration of species builds up in the liquid with time, increasing the initial concentration in the evolved gas. But, also, as the liquid boils away, the ullage space increases and consequently the ullage residence time. Finally, an ullage residence time of such length is reached that the species death rate in the ullage space first

equals and then exceeds the buildup rate, a situation that is reflected by reduced conversion.

Figures 4-12 and 4-13 show the behavior when the reactor was scrammed from 7.2 MW in midrun. As can be seen from Figure 4-12, the parahydrogen concentration rapidly increased after the reactor scram to a level within 0.6% p-H₂ of the composition of the source gas. Figure 4-13 is an expanded-time-scale plot of the first post-scram minute, in which data were recorded at 1-sec intervals.

Figure 4-14 is a plot of liquid volume versus boildown time for the four runs (Nos. 5, 8, 9, and 11) in which the boildown time was sufficient to obtain such data. The slopes of the resulting curves give liquid boiloff rate in ft³/min.

Figure 4-14 Inner-Dewar Boildown Rates

V. ANALYSIS OF RESULTS

5.1 Salient Qualitative Features of the Data

The interpretation of the para- to orthohydrogen conversion data presented in the preceding section is based on the following qualitative considerations.

1. In the case where boildown data were taken immediately after an initial fill (Run 8), the orthohydrogen fraction as a function of boildown showed a distinct maximum (Fig. 4-9).
2. In the case where boildown commenced with the dewar containing a certain amount of LH_2 that had been exposed in previous runs (Run 5), the orthohydrogen concentration fell continuously from an initially high value (Fig. 4-6).
3. The peak orthohydrogen concentration observed in the various runs increased with increasing boiloff rates (small ullage times).
4. The peak orthohydrogen concentration did not seem to be correlated with reactor power level.
5. Substantially more conversion was observed in the case where the conditioner was near the dewar (Sample 1) than in the case where the gas passed through a long tube to a remote conditioner (Sample 2).
6. No correlation was apparent between the amount of conversion and the conditioner temperature.

The first three effects enumerated above indicate that the irradiation of LH_2 produces a free radical that is long-lived in the liquid and that dissociates in the ullage gas (at approximately LH_2 temperature) to a relatively short-lived conversion-causing species. This observation is in accord with the results

of a recent calorimetric experiment reported elsewhere (Ref. 7), which were interpreted to mean that radiation produces an H_3 complex that is stable in LH_2 and highly dissociative in H_2 gas at LH_2 temperature. The fourth consideration listed above is a direct consequence of the fact that conversion is ultimately induced by H atoms which, at high concentrations, disappear by recombination according to the two-body law.

The last two considerations are assumed to reflect the wall recombination of H atoms at low concentrations; this effect is thought to involve the gradual accumulation of an H-atom monolayer on the conditioner and tube walls. The relative complexity of the latter process imposes a limit on the quantitative correlation that can be expected between the proposed theory and the experimental data. Consequently, the model outlined below is considered to be validated by its successful prediction of the degree of conversion for high H-atom concentrations and short boildown times, together with its qualitative conformity with the overall data.

5.2 General Description of Proposed Model

Figure 5-1 is a schematic showing the essential features of the system used in the experiment. There are three major regions of interest: the liquid volume, the ullage volume, and the conditioner volume. The role played by each is briefly described below.

Figure 5-1 Schematic of the Experimental System

5.2.1 Liquid Volume

It is supposed that the irradiation of LH_2 produces the triatomic complex H_3 at a rate corresponding to a G-value for production inferred from the calorimeter experiment (Ref. 7). Although it has always been assumed that such radiation-induced radicals disappear by associative reactions in the liquid phase, both the calorimetric data and the qualitative features of the conversion data indicate that this assumed precursor to conversion is completely stable in LH_2 , at least in the concentrations that accrued in the experiments. Therefore, the accumulation of H_3 in the liquid is limited only by the loss of such molecules through boiling. The rate at which H_3 molecules are vaporized relative to H_2 molecules is described by a second parameter inferred from the calorimetric data, namely, the relative fugacity, or escaping tendency. The mechanics by which the H_3 complex can be formed and stabilized in LH_2 are the subject of a detailed discussion in Reference 7.

5.2.2 Ullage Volume

The calorimetric experiment also indicated that in the gas phase the H_3 complex dissociates rapidly into H atoms and hydrogen molecules through repulsive collisions, in a manner analogous to the behavior of certain nitrogen oxides. The

H atoms so produced immediately start to recombine with each other. It has been shown that for any gaseous H-atom concentrations that could have been realized in the conversion experiments, the effective third bodies for recombination in the ullage space would be H_2 molecules rather than H atoms. Under these conditions the H-atom concentration would ultimately decrease inversely with the time spent by a gas element in the ullage space and, consequently, no meaningful halflife can be assigned to such H atoms.

Prior to the warming of the hydrogen gas in the conditioners or in the tubes leading to them, the H atoms cannot produce any significant amount of conversion owing to the low equilibrium concentration of orthohydrogen corresponding to the low temperature of the ullage space. Therefore, the conversion that occurred must have been due to H atoms that survived recombination long enough to arrive at the warm-gas region.

5.2.3 Conditioner Volume

Once the H atoms arrive in the conditioner they continue to recombine at a rate that tends to be decreased by the decrease in density and probably tends to be increased by the increase in temperature. The total amount of observed conversion is proportional to the product of the H-atom concentration

and the parahydrogen concentration integrated over the time required for the gas to reach the analyzer. The values of the rate constants for recombination and for exchange conversion are discussed in Subsection 5.9.

5.3 Quantitative Description of H₃ Accumulation in LH₂

It is assumed that radiation produces stabilized H₃ radicals in the liquid at a rate designated as P_r (moles/cm³-min). The radicals are lost from the liquid by boiling and, since they are assumed to decompose rapidly in the gas, the H₃ vapor pressure is taken to be zero. Under these conditions, and allowing f to represent the relative fugacity of H₃, the average time spent by an H₃ complex in the liquid is equal to $1/f$ of the average time spent in the LH₂ volume by an H₂ molecule before it is vaporized.

In the case of continuous replenishment of boiling LH₂, which was approximately the situation in the calorimetric experiment, the concentration of H₃ radicals in the liquid, n (moles/cm³), grows according to the relation (applicable to relatively low free-radical concentrations)

$$dn = (P_r - f\beta n)dt \quad (5-1)$$

where β is the fractional rate of boiling of LH₂ (reciprocal of the time required for the container to boil dry in the

absence of replenishment) and t is the time of exposure in minutes. For the case where $n = 0$ when $t = 0$, the solution of Equation 5-1 is

$$n = \frac{P_r}{f\beta} (1 - e^{-f\beta t}) \quad (5-2)$$

In the calorimetric experiments, the heating of the H_2 gas immediately over the liquid surface was found to conform to Equation 5-2 provided that the following values for P_r and f were chosen:

$$P_r(\text{moles/cm}^3\text{-min}) = 4.0 \times 10^{-17} \dot{E} \text{ (ergs/g(H}_2\text{)-h)} \quad (5-3)$$

where $\dot{E}$ is the dose rate in terms of LH_2 energy deposition per hour, and

$$f = 0.37 \quad (5-4)$$

The value of P_r given in Equation 5-3 corresponds to an H_3 radical production factor of $G = 3.3$ radicals/100 eV. In terms of the known radiation-induced production of H atoms in hydrogen gas (Ref. 8) this means that about 20% of the atoms produced by irradiation of the liquid enter into stable H_3 complexes. It is probable that H atoms that fail to form such complexes disappear rapidly from the liquid by three-body recombination. That the relative fugacity f is less than unity is in accord

with the fact that the H_3 radical is more massive than an H_2 molecule.

It will be seen that the above values of P_r and f lead to a reasonable prediction of the observed conversion, so that the theory of free-radical accumulation presented here offers a unified explanation of the calorimetric and conversion data. Alternately, from the standpoint of the conversion data alone, the above values of P_r and f could be regarded as trial parameters that give a quantitative explanation of the data.

Owing to the difficulty in assigning ullage residence times for the fill runs in the conversion experiment, only the boildown runs will be considered here. In this case the continuous-replenishment Equations 5-1 and 5-2 do not apply. Instead, the following equation can be shown to hold for reasonably low H_3 concentrations (n):

$$\frac{dn}{dt} = P_r + \left[\frac{(1-f)\dot{\beta}}{1-\dot{\beta}t} \right] n \quad (5-5)$$

Prior to most of the boildown runs, the dewar was filled while it still contained some LH_2 that had been irradiated in previous runs. Therefore it must be assumed that, in general, at $t = 0$ the liquid contains an initial H_3 concentration n_0 (moles/cm³). The solution of Equation 5-5 with this boundary condition is

$$n = n_0(1-\dot{\beta}t)^{-(1-f)} + \frac{Pr/\dot{\beta}}{2-f} \left[(1-\dot{\beta}t)^{-(1-f)} - (1-\dot{\beta}t) \right] \quad (5-6)$$

Equation 5-6 gives the accumulation of H_3 radicals in a boil-down run where the fractional rate of boiloff is $\dot{\beta}$ and where Pr depends on the dose rate through Equation 5-3. In general, n_0 is a function of the history of exposure and boildown and would be obtained from repeated application of Equations 5-2 and 5-6.

5.4 H-Atom Concentration in the Ullage Gas

The proposed model assumes that as H_3 complexes vaporize they immediately decompose in the gas, producing free H atoms. It is also assumed that the gas in the ullage space rises at such a rate that the H atoms do not diffuse appreciably from one rising volume-element of gas to another (i.e., it is assumed that the time integral of the rate of H-atom recombination in an element is large compared to the time integral of the divergence term in the appropriate diffusion relation). Then, if $[H]_{uo}$ (moles/cm³) designates the H-atom concentration immediately over the liquid surface, it follows from Equation 5-6 that

$$[H]_{uo} = f \frac{\rho_g}{\rho_l} n \quad (5-7)$$

$$[H]_{uo} = f \frac{\rho_g}{\rho_l} n_0 (1-\dot{\beta}t)^{-(1-f)} + f \frac{\rho_g}{\rho_l} \frac{Pr/\dot{\beta}}{2-f} \left[(1-\dot{\beta}t)^{-(1-f)} - (1-\dot{\beta}t) \right]$$

where ρ_g is the density of hydrogen gas at LH_2 temperature and ρ_l is the density of liquid hydrogen.

Equation 5-7 represents the initial condition for H-atom concentration in an element of gas rising over the liquid. Let the time after boiling be designated as t' . Then, if the diffusion of H atoms out of a rising element of gas can be ignored, the decrease in H-atom concentration due to recombination is described by

$$\frac{d[H]_u}{dt'} = -2R_u[H_2]_u [H]_u \quad (5-8)$$

where $[H]_u$ is the H-atom concentration in a rising element of gas t' seconds after the molecules vaporize, $[H_2]_u$ is the H_2 molecule concentration in the ullage, and R_u is the recombination coefficient for H-atom pairs with H_2 as the third body. The solution to Equation 5-8 with $[H]_u = [H]_{u0}$ when $t' = 0$ is

$$[H]_u = \frac{[H]_{u0}}{1 + 2R_u[H_2]_u [H]_{u0}t'} \quad (5-9)$$

In Equations 5-8 and 5-9 it has also been assumed that heterogeneous recombination (wall recombination) in the ullage space can be ignored. This assumption should hold quite well, since wall recombination is known to require an activation energy that is not available at LH₂ temperature (Ref. 9).

5.5 H-Atom Concentration in the Conditioner

The effect of wall recombination in the conditioner and, in the case of Sample 2, the line leading to the conditioner,

cannot in general be ignored, since the temperature is high enough to provide the activation energy for physical adsorption of H atoms. There are, however, two cases in which wall recombination can reasonably be neglected: (a) the H-atom concentration in the conditioner gas can be sufficiently high that homogeneous recombination, which varies as the square of the H-atom concentration, is large compared to heterogeneous recombination, which varies linearly with H-atom concentration; and (b) whenever the flow of gas into the conditioner from the irradiated dewar is interrupted prior to a run, the H-atom monolayer that is responsible for wall recombination would have time to be depopulated by thermal emission and would not be expected to build up immediately after the gas is throttled back into the conditioner line at the start of a run. In either of these cases the H-atom decrease in the conditioner can be treated in a manner analogous to the homogeneous recombination Equation 5-9 .

From Equation 5-9 it is seen that if the time that a gas element spends in the ullage is τ , the initial H-atom concentration of the element in the conditioner is

$$[H]_{co} = \frac{\rho_g(T_c)}{\rho_g(T_u)} \left[\frac{[H]_{uo}}{1 + 2R_u [H_2]_u [H]_{uo} \tau} \right] \quad (5-10)$$

where $\rho_g(T_c)$ is the density of H_2 gas at the temperature of the conditioner and $\rho_g(T_u)$ is the density of H_2 gas in the ullage. Then, on the assumption of homogeneous recombination in the conditioner, the H-atom concentration of a gas element that has spent a time t'' in the conditioner is, in analogy to Equation 5-9, given by

$$[H]_c(t'') = \frac{[H]_{co}}{1 + 2R_c[H_2]_c[H]_{co} t''} \quad (5-11)$$

where $[H_2]_c$ is the H_2 molecule concentration in the conditioner and R_c is the recombination coefficient for the temperature of the conditioner. Equation 5-11 gives the instantaneous concentration of H atoms for the calculation of the rate of para- to orthohydrogen conversion in an element of gas inside the conditioner.

5.6 Reaction Rate for p- H_2 to o- H_2 Conversion

It can be assumed that the conversion of one hydrogen modification to another in the conditioner is due solely to H-atom exchange. In principle, there should be some back-conversion from ortho- to parahydrogen due to magnetic interactions between H atoms and o- H_2 molecules. But even though the magnetic-conversion efficacy of an H atom exceeds that of another o- H_2 molecule by the square of the ratio of their respective magnetic moments, namely, by a factor of about

$(1/2 \cdot 1840)^2$, multiplication of this value by the homogeneous rate constant for magnetic conversion shows that the H-atom concentration in the conditioner would have to exceed the estimated values of $[H]_c$ by at least an order of magnitude for magnetic conversion to be noticeable. Therefore, the rate at which o-H₂ accumulates in the conditioner can be expressed in terms of k , the rate constant for the formation of an H-H₂ complex. Let $[H_2]_p$ designate the parahydrogen concentration in the conditioner and let $[H_2]_o$ designate the orthohydrogen in the conditioner. Then the rate of increase of orthohydrogen is given by

$$\frac{d[H_2]_o}{dt''} = 3/4k[H]_c[H_2]_p - 1/4k[H]_c[H_2]_o \quad (5-12)$$

where the first term represents the rate of conversion of parahydrogen to orthohydrogen and the second term represents the rate of back-conversion. The following relation holds, of course, between $[H_2]_p$ and $[H_2]_o$:

$$[H_2]_o = [H_2]_c - [H_2]_p \quad (5-13)$$

Substitution of this expression for $[H_2]_o$ and the expression for $[H]_c(t'')$ given in Equation 5-11 into Equation 5-12 gives the rate of orthohydrogen increase in a gas element in the conditioner at a time t'' after it has warmed to conditioner

temperature. It is assumed that the warming process is almost instantaneous, so that the temperature dependence that certainly applies to k can be ignored.

Integration of Equation 5-12 gives the amount of orthohydrogen produced in an element of gas that has been in the warm region for a time θ . The time θ should include the time spent in the line running to the analyzer, although it is probable that the effect of wall recombination in this line renders the homogeneous recombination assumption implicit in Equation 5-11 invalid for the relatively short time required for the gas to pass from the conditioner to the analyzer. Solution of Equations 5-12, 5-13, and 5-11 gives for the orthohydrogen concentration after a conditioner time θ ,

$$[H_2]_o = 3/4[H_2]_c \left\{ 1 - \left[1 + 2R_c[H_2]_c [H]_{co}\theta \right]^{-k/2R_c[H_2]_c} \right\} \quad (5-14)$$

where the minuscule concentration of orthohydrogen in the gas entering the conditioner has been neglected.

5.7 Fractional Conversion to "Normal" Hydrogen

"Normal" hydrogen is defined as a mixture of orthohydrogen and parahydrogen in the respective proportions of 3/4:1/4. Thus, if the mixture leaving the conditioner were normal, the orthohydrogen concentration would be $3/4[H_2]_c$. It is therefore convenient to define the "fractional conversion to normal hydrogen" as

$$P(\theta) = [H_2]_0 / 3/4 [H_2]_c \quad (5-15)$$

Equations 5-14 and 5-15 give the desired relation for the prediction of fractional conversion to normal hydrogen in the experiment:

$$P(\theta) = 1 - \left[1 + 2R_c [H_2]_c [H]_{co} \theta \right]^{-k/2R_c [H_2]_c} \quad (5-16)$$

Equation 5-16 shows that, in principle, an arbitrarily small concentration, $[H]_{co}$, of H atoms entering the conditioner would eventually complete the conversion if the time θ were made large enough. This would never occur in practice since wall recombination would render Equation 5-11 invalid when the concentration $[H]_c(t'')$ dropped below a certain minimum value. The same effect implies that Equation 5-16 should overpredict the fractional conversion to normal hydrogen except in the cases where (a) the initial concentration $[H]_{co}$ is relatively high and/or (b) an H-atom monolayer has not had time to build up on the conditioner wall.

Equation 5-16 can be expressed in a useful approximate form that is expected to hold under the conditions of the experiment and under the conditions of validity of Equation 5-16 itself. If it is assumed that

$$2R_c [H_2]_c [H]_{co} \theta \ll 1 \quad (5-17)$$

then it is easily shown that

$$P(\theta) \simeq 1 - e^{-k[H]_{CO}\theta} \quad (5-18)$$

This result is independent of R_c , the coefficient for H-atom recombination at the conditioner temperature. Values of $[H]_{CO}$ calculated from Equation 5-10 and the value of R_c estimated in Subsection 5.9 indicate that the inequality (5-17) is realized, so that Equation 5-18 should give about the same result as Equation 5-16. Comparisons between theory and experiment can now be made on the basis of Equations 5-16 or 5-18 and Equation 5-10, which gives the H-atom concentration entering the conditioner.

5.8 Qualitative Conformity of Theory and Experiment

Equations 5-16 and 5-18 show that the fractional conversion to normal hydrogen always increases as $[H]_{CO}$ increases, as would be expected. Therefore, the significant qualitative features of the experimental data listed in Subsection 5.1 can be examined in terms of the variation of $[H]_{CO}$ due to its dependence on $[H]_{UO}$ shown in Equation 5-10. Both $[H]_{UO}$ and τ , the time in ullage, are functions of t , the time after initiation of boildown. The t dependence of $[H]_{UO}$ is given in Equation 5-7. The average time τ that an element of gas spends in the ullage space is given by

$$\tau = \frac{\rho_g}{\rho_l} \left[\frac{1 - \phi}{\phi} + \beta t \right] \frac{1}{\beta} \quad (5-19)$$

where ϕ is the fraction of the dewar that is filled with liquid at the start of a boil-down run. Equations 5-7 and 5-19 show that both $[H]_{u0}$ and τ increase monotonically as a function of the boil-down time t . Then Equation 5-10 shows that if $[H]_{u0}$ starts out with an initial value of zero, a maximum will occur in $[H]_{c0}$ as a function of the boil-down time. On the other hand, if the radical concentration in LH_2 at the start of the run, n_0 , is not zero (see Equations 5-6 and 5-7) the relative rate of increase in $[H]_{u0}$ may be too slow for Equation 5-10 to show a maximum. Equations 5-7, 5-10, and 5-19 taken together also indicate that the value of $[H]_{c0}$ for a fixed value of t increases with increasing values of the fractional boil-off rate $\dot{\beta}$. These results are in accord with the first three attributes of the data listed in Subsection 5.1.

The appearance of $[H]_{u0}$ in both the numerator and denominator of Equation 5-10 explains the insensitivity of the conversion rates to power level. Since the dose rate enters only through $[H]_{u0}$, it is clear that $[H]_{c0}$ will be entirely independent of $\dot{E}$ once τ becomes large enough for the following relation to hold:

$$1 \ll 2R_u[H_2]_u[H]_{u0}\tau \quad (5-20)$$

Thus, the decrease in $[H]_{co}$ with τ always converges onto the asymptotic form

$$[H]_{co} = \frac{\rho_g(T_c)}{\rho_g(T_u)} \frac{1}{2R_u[H_2]_u \tau} \quad (5-21)$$

which is independent of the dose rate $\dot{E}$. Although the peak rate of H-atom entry into the conditioner would be expected to vary slightly with dose rate, the sensitivity would be nowhere near a linear dependence on $\dot{E}$. This result is a direct consequence of assuming that H atoms disappear by homogeneous recombination. If the conversion-causing species decayed with a constant halflife, the concentration entering the conditioner would always be proportional to $[H]_{uo}$ and hence to $\dot{E}$ through the parameter P_r .

The fact that less conversion was observed in the case of Sample 2 than in Sample 1 can only be the result of wall recombination, since the lines leading to the conditioners were known to be at near room temperature and since Equations 5-16 and 5-18 do not differentiate between a conditioner and a line. The quantitative comparisons will show that in some cases wall recombination was significant even inside the conditioner for Sample 1. The fact that the conversion was not increased by increasing the conditioner temperature is also tentatively attributed to wall recombination.

Since wall recombination requires an activation energy, it is reasonable to assume that the rate of disappearance of H atoms increases with increasing temperature. The fact that the peak conversion in one of the high-temperature runs (Run 9) was equal to that in Run 8 is probably accidental and should be considered in context with the fact that the ortho-hydrogen concentration in Run 9 for small values of t was depressed relative to that of Run 8. Unfortunately, the level of confidence in the theory of wall recombination does not warrant a quantitative analysis of this effect at the present time.

5.9 Reaction Rate Constants

An attempt will be made at an a priori calculation of some of the conversion data using Equation 5-18 and the values of P_r and f inferred from the calorimetric data. For this purpose two rate constants are required, namely, R_u , the recombination coefficient for H atoms in the ullage space with H_2 molecules as third bodies, and k , the rate constant for H-atom exchange.

Although the recombination constant for H atoms with H atoms as third bodies has been satisfactorily measured, only an upper bound has been placed on the recombination constant for H_2 molecules as third bodies. (An early experimental value given by Steiner in Reference 10 is now considered to be

impossibly high.) On the basis of the equilibrium constant for hydrogen dissociation, Lewis and von Elbe (Ref. 11) have, in effect, shown that at normal temperature the recombination coefficient has an upper bound of

$$R_C \approx 1 \times 10^{14} \text{ cm}^6/\text{mole}^2\text{-sec}$$

The number on the right would actually represent the rate constant inferred from dissociation data if it could be assumed that every $\text{H}_2\text{-H}_2$ collision in which the relative kinetic energy exceeded the H_2 dissociation energy actually produced a dissociation. For the purpose of the present calculations, an estimate of R_C has been made by estimating the actual dissociation probability in terms of steric factors.

For collision energies only slightly in excess of the dissociation energy, dissociation can occur only if the H_2 molecule that is not dissociated is also not excited to energetic vibrational or rotational states. This requires that one of the two colliding molecules be aligned within a small solid angle about the line of collision and that the other lie in a plane whose normal lies within a small angle about the line of collision. On the basis of the known inertial moments of the H_2 molecule and a semiclassical model for excitation, it is estimated that the steric factor for the first molecule is about 1/50 and the steric factor for the second is about 1/10.

If these estimates are valid, only about one collision in 500 in which the energy exceeds the H_2 dissociation energy will actually cause dissociation. In this case the equilibrium constant for dissociation implies that

$$R_c \approx 2 \times 10^{11} \text{ cm}^6/\text{mole}^2\text{-sec}$$

Then, on the assumption that the recombination coefficient varies as $T^{\frac{1}{2}}$, the recombination coefficient in the ullage space should be about

$$R_u \approx 0.5 \times 10^{11} \text{ cm}^6/\text{mole}^2\text{-sec}$$

Although the method used to obtain this value is not entirely satisfactory, the result will have to suffice for the present calculations.

The rate constant for exchange conversion has been calculated by Shavitt (Ref.12), who used two different sets of parameters and compared the results with two different sets of experimental data. At 540°R the comparisons are as follows:

$$k = \begin{cases} 8.1 \times 10^8 & (\text{calc 1}) \\ 3.9 \times 10^8 & (\text{calc 2}) \\ 1.4 \times 10^8 & (\text{exp 1}) \\ 2.0 \times 10^8 & (\text{exp 2}) \end{cases} \quad \text{cm}^3/\text{mole-sec}$$

Shavitt analyzed the experimental methods and concluded that the $3.9 \times 10^8 \text{ cm}^3/\text{mole-sec}$ value was the most realistic. Consequently, this value, corrected for conditioner temperature

slightly below 540°R, will be used. The corrected value is

$$k = 3.6 \times 10^8 \text{ cm}^3/\text{mole-sec}$$

The only other parameters required for the calculations are ρ_g/ρ_ℓ , the ratio of the density of H₂ gas at saturation to LH₂ density; $\rho_g(T_c)/\rho_g(T_u)$, the ratio of H₂ gas density in the conditioner to H₂ gas density in the ullage; and $[H_2]_u$, the molar density of H₂ gas in the ullage. These values have been obtained from standard sources and are included in the following summary of parameters and symbols. The independent variables of the experiment are $\dot{E}$, $\dot{\beta}$, and ϕ , which are known from dosimetry and liquid-level data, and t , the increasing time of boildown in a given run.

5.10 Summary of Parameters and Symbols

The following parameters are employed for the calculation of $P(\theta)$, the fractional conversion to normal hydrogen, by Equation 5-18:

$\dot{E}$ = dose rate in terms of energy deposition in hydrogen [ergs/g(H₂)-h]

$\dot{\beta}$ = fractional boiloff rate, the reciprocal of time to boil dry from initial fill (1/min)

ϕ = initial fill fraction

P_r = assumed production constants for H₃ radicals in LH₂; see Eq. 5-3 (moles/cm³-min)

f = assumed relative fugacity of H₃ radicals in LH₂ (=0.37)

t = boildown time from initial fill (min)

$[H]_{uo}$ = initial H-atom concentration in ullage; see Eq. 5-7 (moles/cm³)

$[H_2]_u$ = concentration of H₂ in ullage (0.62 x 10⁻³ mole/cm³)

τ = average time in ullage; Eq. 5-19 x 60 sec/min (sec)

$[H]_{co}$ = initial H-atom concentration in conditioner; see Eq. 5-10 (moles/cm³)

θ = time in conditioner (8 to 10 sec)

ρ_g/ρ_ℓ = ratio of density of H₂ vapor to density of LH₂ (=1/57)

$\rho_g(T_c)/\rho_g(T_u)$ = ratio of density of conditioner gas to density of ullage gas (=1/14)

R_u = assumed H-atom recombination coefficient (0.5 x 10¹¹ cm⁶/mole²-sec)

k = assumed H-H₂ reaction rate constant at $\approx 540^\circ R$ (3.6 x 10⁸ cm³/mole-sec)

The fractional conversion to normal hydrogen has been calculated by the above method for the two boildown runs in which the conditions for the validity of Equation 5-18 should have been most nearly met.

5.11 Calculation of Conversion in Run 5

Run 5 is considered because it was in this run that the maximum fraction of conversion to normal hydrogen in a boildown run was observed. Since two runs in Session 1 had been made

prior to Run 5, and since complete boildown seems not to have been achieved in either, it must be assumed that the initial H_3 radical concentration in the LH_2 was not zero at the start of Run 5. Although a detailed history of the first two runs is not available, a rough estimate of the initial concentration n_0 is made in the following way.

The dose rate in the first two runs was about $\dot{E} = 2 \times 10^9$ ergs/g(H_2)-h. It is estimated that in each the liquid level dropped to a fill fraction of about 0.3 prior to refill. The fractional rate of boiloff was about $\dot{\beta} = 0.1/\text{min}$. An iterative use of these values in Equation 5-6 leads to the conclusion that at the start of Run 5 the concentration of H_3 molecules in the LH_2 must have been on the order of

$$n_0 \approx 1 \times 10^{-6} \text{ mole/cm}^3 \quad (\approx 3 \times 10^{-5} \text{ molar})$$

The corresponding value of $[H]_{uo}$, the initial concentration of H atoms in the ullage space immediately over the liquid, is roughly

$$[H]_{uo}(t = 0) \approx 1 \times 10^{-8} \text{ mole/cm}^3 \quad (\approx 1 \times 10^{-5} \text{ molar})$$

Therefore, the values of $[H]_{uo}(t)$ for Run 5 have been calculated by replacing the first term on the right of Equation 5-7 by

$$\frac{\rho_g}{\rho_\ell} = n_0(1 - \beta t)^{-(1-f)} = (1 \times 10^{-8})(1 - \beta t)^{-(1-f)} \text{ mole/cm}^3$$

As it turned out, the use of the above value gave a good prediction of the observed conversion for small boildown times t , where the second term in Equation 5-7 was negligible. Owing to the rough manner in which n_0 was obtained, this agreement must be considered as partly accidental and the Run 5 calculations cannot be regarded as wholly a priori. Nevertheless, the order of magnitude of the assumed n_0 is completely consistent with the theory, and the change in the calculated amount of conversion as $(1 - \beta t)^{-(1-f)}$ decreased and the second term in Equation 5-7 increased is in reasonable agreement with the experimental data. It can therefore be claimed that the use of the above value of $[H]_{u0}(t = 0)$ represents a fair application of the theory.

The fractional conversion to normal hydrogen in Run 5 as a function of boildown time has been calculated from the above value of $[H]_{u0}(t = 0)$ and the empirically determined parameters

$$\dot{E} = 2.4 \times 10^9 \text{ ergs/g(H}_2\text{)-h}$$

$$\beta = 0.0906/\text{min}$$

$$\phi = 0.92$$

Equation 5-3 gives for the free-radical production factor in LH_2

$$P_r = 0.96 \times 10^{-7} \text{ mole/cm}^3\text{-min}$$

In order to convey the orders of magnitude of the time in ullage, the H-atom concentration in the ullage gas, and the H-atom concentration in the conditioner, Table 5-1 lists, for some representative values of the boildown times t , some values of τ , calculated from Equation 5-19; $[H]_{uo}$, calculated from Equation 5-7; and $[H]_{co}$, calculated from Equation 5-10.

Table 5-1

REPRESENTATIVE ULLAGE TIMES AND H-ATOM CONCENTRATIONS
IN RUN 5

$t(\text{min})$	$\tau(\text{sec})$	$[H]_{uo} \text{ (mole/cm}^3\text{)}$	$[H]_{co} \text{ (mole/cm}^3\text{)}$
0.1	1.113	1.012×10^{-8}	4.256×10^{-10}
0.5	1.533	1.061×10^{-8}	3.773×10^{-10}
1.0	2.058	1.126×10^{-8}	3.300×10^{-10}
2.0	3.108	1.267×10^{-8}	2.630×10^{-10}
5.0	6.258	1.847×10^{-8}	1.620×10^{-10}

Table 5-1 shows that the time in ullage is of the order of seconds. The decrease as a function of boiloff time is due, of course, to the fact that the accessible ullage volume increases as the LH₂ level drops. The H-atom concentration over the liquid is of the order of $10^{-8} \text{ mole/cm}^3$ (10^{-5} molar)

and increases as the liquid boils down. This increase is the result of two separate effects: the assumed production of H_3 radicals by radiation and the assumed fractionation effect resulting from the fact that the relative fugacity of the radicals is less than unity. The H-atom concentration in the conditioner is of the order of 10^{-10} mole/cm³ (10^{-6} molar) and, in this case where $n_0 \neq 0$, decreases monotonically with increasing boil-down time. This means that the increased disappearance of H atoms due to increasing time in ullage is more than enough to override the increase in $[H]_{uo}$. If n_0 had been taken as zero, a maximum in $[H]_{co}(t)$ would have occurred.

The ratio of H atoms to H_2 molecules in the warm conditioner gas is on the order of 10^{-6} . This value is small from the standpoint of population but quite large from the standpoint of the concentration of atomic impurities required for conversion. That the fractional conversion to normal hydrogen can be computed from Equation 5-18 rather than from Equation 5-16 is seen by substituting the following values into the inequality 5-17: $R_c = 2 \times 10^{11}$ cm⁶/mole²-sec, $[H_2]_c = 0.45 \times 10^{-4}$ mole/cm³, $[H]_{co} = 10^{-10}$ mole/cm³, $\theta = 10$ sec. Since the quantity on the left of 5-17 is only about 0.02, it

follows that Equation 5-18 holds for the fractional conversion to normal hydrogen.

The fractional conversion to normal hydrogen $P(\theta)$ for Run 5 has been calculated from Equation 5-18 with θ taken to be 10 sec. The results are compared with the experimental values for Sample 1 in Figure 5-2. It is seen that the agreement is quite good except at the one point corresponding to a boildown time of 1.2 min. Whether this represents a bad experimental point or a structure that is not accounted for in the theory cannot be ascertained at present. The failure of wall recombination to depress the experimental points is also unexplained, but may be due to relatively clean conditioner surfaces produced by the action of H atoms in the first two runs.

5.12 Calculation of Conversion in Run 8

The only other run to which theory has been applied is Run 8. It was chosen for consideration since it represents the only case in which part of the liquid had not been exposed in previous runs. Thus, n_0 can be set equal to zero in Equation 5-6, and $\dot{E}$, $\dot{\beta}$, and ϕ evaluated as follows:

$$\dot{E} = 1.6 \times 10^9 \text{ ergs/g(H}_2\text{)-h}$$

$$\dot{\beta} = 0.0285/\text{min}$$

$$\phi = 0.75$$

Figure 5-2 Experimental and Calculated Fractional Conversion to Normal Hydrogen

From Equation 5-3 the free-radical production factor is

$$P_r = 0.64 \times 10^{-7} \text{ mole/cm}^3\text{-min}$$

Representative ullage times and concentrations in the ullage and conditioner, calculated from Equations 5-19, 5-7, and 5-10, are listed in Table 5-2. It is seen that the H-atom concentrations are more than an order of magnitude less than in Run 5.

Table 5-2

REPRESENTATIVE ULLAGE TIMES AND H-ATOM CONCENTRATIONS
IN RUN 8

t(min)	τ (sec)	$[H]_{uo}$ (mole/cm ³)	$[H]_{co}$ (mole/cm ³)
0.5	12.82	0.208×10^{-9}	1.27×10^{-11}
1.0	13.35	0.417×10^{-9}	2.22×10^{-11}
2.0	14.40	0.843×10^{-9}	3.44×10^{-11}
5.0	17.55	2.173×10^{-9}	4.60×10^{-11}
6.0	18.60	2.638×10^{-9}	4.66×10^{-11}
7.0	19.65	3.115×10^{-9}	4.64×10^{-11}
10.0	22.80	4.631×10^{-9}	4.40×10^{-11}

In this case the H-atom concentration entering the warm gas reaches a maximum value at about $t = 6$ min and declines slowly thereafter, which results from the fact that $n_0 = 0$.

The fractional conversion to normal hydrogen in Run 8 has been calculated from Equation 5-18 using $\theta = 10$ sec. These results are also shown in Figure 5-2. It is seen that the calculated values are in excellent agreement with the experimental data for the first 4 min of boildown. Thereafter, the experimental data drop sharply to a value that is a factor of about 3 below the calculated results. The reason for this sharp decline is thought to be the accumulation of a monolayer of H atoms on the conditioner walls. It is quite possible that the growth of such a layer is nonlinear because of energy transfer to H atoms already adsorbed. Under these conditions H-atom recombination would undergo a sudden increase once a certain critical wall population was achieved. In any event, the ability of the theory to give order-of-magnitude agreement for both Runs 5 and 8 is an encouraging sign that both the overall model and the free-radical production parameters inferred from the calorimetric data are essentially valid.

5.13 Summary of Analysis

Calculations of the conversion of parahydrogen to orthohydrogen for the conditions of two of the experimental runs have been performed on the assumption that conversion is due to H-atom exchange in the conditioners. The origin of the

H atoms is assumed to be the radiation-induced production of a hydrogen radical that is long-lived in the liquid and that rapidly dissociates to atomic hydrogen in the vapor phase. The parameters for the rate of production and vaporization of the parent radical were obtained from a calorimetric experiment in which it was concluded that the H-atom parent is an H_3 complex that is virtually stable as long as it remains in the liquid. The H atoms produced by the decomposition of such radicals in the gas phase are assumed to be subject to homogeneous recombination with H_2 molecules as third bodies. The three-body recombination coefficient has been estimated by the application of steric factors to data on the degree of dissociation of hydrogen at elevated temperatures.

The amount of exchange conversion induced by H atoms that survive recombination long enough to reach the warm region where conversion is possible has been calculated using a published rate constant for H- H_2 exchange. Order-of-magnitude agreement was obtained between the calculated conversion and both of the experimental runs considered. The dependence of the degree of conversion on boildown rates and power level was reasonably good, although it appears that the experimental data were depressed by the heterogeneous recombination of atomic

hydrogen on the conditioner walls, an effect that was neglected in the calculations. On the basis of the overall conformity of the theoretical results with the data, it is tentatively assumed that the model is essentially correct, although confirmation cannot be made until an experiment is run in which better control of such variables as boiloff rate and gas temperature is possible.

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APPENDIX A
EQUIPMENT AND INSTRUMENTATION

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APPENDIX A

EQUIPMENT AND INSTRUMENTATION

The reactor and the GTR Radiation Effects Testing System are described in Appendix C. The major pieces of apparatus required for the test are listed below. Each is then subsequently described in separate subsections.

1. Irradiation Dewar
2. Conditioner
3. Hydrogen Transfer System
4. Para-Orthohydrogen Analyzer
5. Miscellaneous Instrumentation

The dewar, sample lines, and conditioners are constructed entirely of aluminum. Principally by virtue of its short halflives for artificially induced radioactivity and its light weight and high strength, aluminum is considered to be an ideal material for construction of hardware to be used in irradiation tests. It is a fortunate coincidence that aluminum is also ideal from the standpoint of being a noncatalyst for the $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ reaction.

A characteristic of the metal is that upon exposure to air a heavy oxide film forms almost immediately. Any paramagnetic substance is a catalyst for the $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ reaction

and its magnetic susceptibility is an index of the catalytic strength, although other factors such as available surface area are important too. Because aluminum-oxide has a negative value of magnetic susceptibility it is diamagnetic and, hence, a noncatalyst. Use of aluminum wherever possible therefore minimizes the possibility of conversion unrelated to nuclear radiation.

In this regard, every effort was made to ensure that pertinent surfaces exposed to hydrogen were kept free of contaminants, again to minimize the possibility of conversion unrelated to nuclear radiation.

A.1 Irradiation Dewar

The irradiation dewar has two vessels for liquid, one contained within the other. The inner vessel contains the active hydrogen and can be either totally or partially immersed in the liquid contained by the outer vessel. The vessels are isolated one from the other; that is, there is no interchange of hydrogen between the two vessels. Figures A-1 through A-4 are photographs of the dewar in various stages of assembly and will be helpful in following the ensuing discussion of the details.

Figure A-1 Irradiation Dewar with Inner Liquid Vessel Attached

Figure A-2 Irradiation Dewar with Liquid Vessels and Shroud Doors Removed

Figure A-3 Irradiation Dewar: Installation of the Inner Vessel in the Outer Vessel

Figure A-4 Closeup of Shrouded Section

A-1.1 Inner Vessel

As can be seen from the figures the dewar has two volumes for liquid hydrogen, one located within the other. The inner vessel is the volume from which gas for analysis is extracted. Figure A-1 affords the best view of the inner vessel, which has a liquid capacity of 1.97 ft^3 ($\approx 15 \text{ gal}$).

In this experiment the test article is the cryogen itself; therefore, in order to minimize the possibility of biasing events, the only items permitted in the inner vessel were those necessary for control of the cryogen. These items, visible in Figure A-2, consist of a fill line, an aluminum-jacketed electric heater, and a liquid probe. A pressure probe, also visible in the photograph, penetrates the inner vessel lid but does not extend beyond. All of these penetrations are welded at the lid to ensure a leak-tight seal.

The inner vessel is suspended from the lid of the outer vessel by the inner vessel's exhaust tube (see Fig. A-1), which is located on the axis of symmetry. All gas evolved in the inner vessel is exhausted through this tube. At the top end of the tube, inside the shrouded volume

(discussed later), are located the two sample taps through which gas is extracted for analysis.

Figure A-3 shows the inner vessel being lowered into the outer vessel. When in place, the inner vessel is suspended inside the outer vessel with a clearance of approximately 3 in. between the vessel walls.

A.1.2 Outer Vessel

The vacuum-jacketed outer vessel is entirely conventional in design. Its sole purpose is to provide a cold environment for the inner vessel. Depending upon the fill level of the outer vessel, the inner vessel can be either totally or partially immersed in liquid hydrogen.

When the inner vessel is completely immersed, the heat loads on the inner vessel are substantially reduced. Thermal heat leak to the inner is reduced essentially to zero, and approximately one-half the nuclear heating of the inner vessel (but not its contents) is carried away by boiling of the liquid in the outer vessel. The advantages accruing from the two-vessel arrangement are twofold: (1) the slower boiling of the inner vessel's contents permits longer irradiation periods for a given sample quantity, and (2) the ullage

gas in the inner vessel is maintained at a temperature much closer to that of liquid hydrogen than would otherwise be possible.

A.1.3 Shroud

All connections to the dewar penetrations are made within the shroud located on top of the dewar. The shroud is continuously purged with helium so that any small leak that may develop at the connections is diluted and carried away.

The shroud, with access doors removed, can be seen in all the photographs of the dewar; but Figure A-4, a closeup view, provides the best detail of the mode of connection.

The dewar is penetrated by five hydrogen-carrying lines - two fill and three exhaust. Connection at the dewar is to the five stubs visible in Figure A-4. These stubs are flange-bolted, using lightly silicon-greased gaskets, over openings in the outer dewar lid, which is also the shroud floor. The flexible external lines terminate in a rigid flanged stem, and the stem itself terminates in a suitable fitting (Linde bayonet fittings for fill lines, AN unions for exhaust lines). These stems are introduced through holes in the shroud top, and the gasketed flanges are bolted as the threaded terminals are simultaneously drawn tight. Expansion

bellows, visible as the convoluted sections in the photograph, are used to accommodate small flange-to-terminal mismatches as well as differential thermal contraction.

The electrical connections are also visible in Figure A-4. A single hermetic connector admits all instrumentation wiring (thermocouples and 0.1-watt liquid-level resistors). Inside the shroud, the instrumentation harness is divided into two parts: one for the inner vessel and one for the outer vessel. From there, entry into both vessels is obtained in like fashion (hermetic connectors) through the appropriate exhaust tube.

Power (ac) for the inner-dewar heater is admitted to the shroud through a separate hermetic connector. The wiring is then led directly to the heater through the heater jacket, which is a continuous run of aluminum tubing starting 1.5 in. above the shroud floor. The tube is potted with epoxy resin to minimize the chance of hydrogen being exposed to a possible arcing short in the heater.

In the center of Figure A-4, the taps for Samples 1 and 2 are visible. One-fourth-inch fittings are threaded into bosses welded to the exhaust-tube sides. Two 0.25-in. aluminum lines, looped to accommodate thermal contraction,

lead to bulkhead fittings welded into the shroud wall where the two gas sampling lines leading to the gas analyzer are attached.

At the top right-hand portion of Figure A-4, the exit port for the helium purge is visible. Gas exiting through this port (≈ 2 cfm) is eventually vented to the atmosphere through an unfired stack located at the north end of the facility complex. Helium is supplied through a 0.5-in. line from a 100,000-ft³ capacity tube trailer.

Two gasketed 0.25-in.-thick aluminum access doors complete the enclosure. When the doors are in place and all connections are properly made, escape of hydrogen into the irradiation test cell is highly unlikely.

A.2 Conditioner

Each of the two primary sample lines (Sample 1 and Sample 2) has an enlargement called a conditioner which functions to provide the requisite high-temperature region. Both conditioners are identical. Each is a 2-in.-i.d. by 2-ft-long cylinder which is wrapped with an electric tape-heater and thermal insulation. Temperatures of 1100°R, monitored by thermocouples located near either end and controlled from the gas analyzer can be easily attained.

One conditioner is mounted on the irradiation dewar in order to minimize line length between conditioner and dewar ullage and, as a consequence, is in the intense radiation field. The other unit is located further from the dewar and is not in an intense radiation field.

From the standpoint of conversion of parahydrogen to orthohydrogen, 240°K (430°R) can be regarded as a high temperature. Even at 140°K (250°R) the obtainable conversion is within 5% parahydrogen of the maximum, i.e., the equilibrium concentration at 140°K is 30% parahydrogen and 70% orthohydrogen. The excessive temperature capability of the conditioner is for the purpose of securing a high heat flux into the gas and, hence, more rapid warming.

It is emphasized that high temperature has nothing to do with initiating conversion; in the absence of a catalyst the temperature of the gas can be increased up to about 2000°K (or 3600°R , where dissociation effects appear) and no conversion will occur.

A.3 Hydrogen Transfer System

A.3.1 Bulk Hydrogen

The diagram of the Hydrogen Transfer System shown as Figure A-5 approximates the actual physical layout.

Figure A-5 Gas Transfer System

Liquid parahydrogen is fed from a 12,000-gal transport trailer to a cryogen manifold. The cryogen is then supplied to the dewar through 90 ft of 0.75-in.-i.d. vacuum-jacketed stainless-steel flexible line. A separate line is used for each liquid container of the dewar, one for the inner and one for the outer. The supply is controlled by a Liquid-Level System, which is discussed in Subsection A.5.1.

All effluent from the outer vessel and virtually all from the inner vessel is exhausted into the facility's stationary hydrogen exhaust system by means of 50-ft uninsulated 1.25-in.-i.d. flexible lines. One such exhaust line is used for the inner vessel; two are required for the outer vessel because of the high boiloff rates experienced at 10-MW reactor power. Release to the atmosphere is ultimately accomplished through a natural-gas-fired burn stack located at the southeast corner of the facility.

A.3.2 Sample Gas System

Sample 1 and Sample 2. Three sample lines, designated Sample 1, Sample 2, and Sample 3, are used to obtain gas for analysis. The two lines of primary importance, Sample 1 and Sample 2, are tapped into the shrouded section of the inner

vessel exhaust tube as described in Subsection A.1.3. Each of these lines is 70 ft long and leads directly to the sample side of the gas analyzer, which is located in the control room. Both lines are made of nominal 0.25-in.-diam (0.190 i.d.) aluminum-alloy tubing as a precaution against system catalysis.

As has been previously stated, the sole difference in these lines is the location of the conditioner (high-temperature region). For Sample 1, the conditioner is located 2 ft downstream of the takeoff tap. For Sample 2, the conditioner is located 50 ft downstream of the takeoff tap.

Sample 3. The Sample 3 line is tapped into the main exhaust system at the union of the flexible line with the stationary hydrogen exhaust system. Twenty feet of aluminum-alloy tubing lead directly from the top to the sample side of the gas analyzer. This third sample is obtained from precisely the same point as in the exploratory experiment and is for the purpose of determining if the conversion observed in that experiment might have occurred in the 50-ft section of 1.25-in. stainless-steel flexible line connecting the dewar to the stationary exhaust system.

Reference Gas. Reference gas (standard for comparison) is obtained directly from the transport trailer ullage via the trailer gas recovery port and is piped to the reference side of the gas analyzer through 80 ft of 0.25-in. copper refrigeration tubing.

Excess Sample Return. Each of the three sample lines is capable of delivering up to 40 scfh (standard cubic feet per hour) of hydrogen to the analyzer. Although desirable from the standpoint of reducing transit time between dewar and analyzer, such high flow rates are far in excess of the analyzer demand, which is only 0.33 scfh. The excess over analyzer requirements is returned to the main exhaust stream by means of bypass valves located on the analyzer gas-flow control panel.

Immediately downstream of the analyzer the three return lines are manifolded into a common 0.5-in. copper line which is tied into the inner-vessel section of the main exhaust stream immediately downstream of a hand valve. By throttling this latter hand valve, a suitable pressure drop can be obtained to secure an adequate amount of gas through the sample stream.

A.4 Para-Orthohydrogen Analyzer

The gas analyzer (Fig. A-6) is patterned after continuous flow devices described by D. H. Weitzel et al. (Refs. 13,14) and operates by comparing the thermal conductivity of a sample stream of hydrogen with that of a stream of hydrogen having a known parahydrogen concentration. This is accomplished by comparing the resistances of four gas-stream-exposed filaments connected as the four arms of a Wheatstone-bridge in a unit called a thermal conductivity cell (T/C cell). The filament temperatures, and therefore the resistances, are related to the conductivities of the gases passing over them. Because the thermal conductivity of hydrogen varies directly with parahydrogen concentration, the degree of bridge unbalance caused when the sample and reference gases are simultaneously passed over opposing legs of the bridge can be directly related to the parahydrogen concentration of the sample stream.

Figure A-7 is a schematic of the T/C cell bridge circuit. With the cell operating in an ice bath, an excitation potential of 7.5 V produces a bridge current of 300 mA. Although a wide latitude is permissible in parameter selection, the 300 mA current value, which is 75% of the maximum value

Figure A-6 Para-Orthohydrogen Analyzer

Figure A-7 Thermal-Conductivity-Cell Bridge Circuit

Figure A-8 Analyzer Instrumentation

recommended by the manufacturer, gives a good compromise between filament service life and signal strength.

Figure A-8 is a block diagram of the instrumentation. The power-supply control unit has been modified to incorporate a fine-balance potentiometer, a signal-excitation selector switch, and a calibration resistor.

The fine-balance potentiometer facilitates achievement of a good bridge null. Bridge excitation voltage can be displayed on the digital voltmeter (DVM) by means of the signal-excitation switch, thereby permitting far more precision in setting bridge current than can be obtained by using the bridge-current panel meter alone.

Bridge unbalance is displayed on the DVM in millivolts, and recorded, on command, by the printer at the rate of 2 lines/sec. For this experiment the output was paralleled to the Dymec Data Acquisition System (DAS) shown in Figure A-9. The DAS was additionally programmed to cyclically record T/C cell temperature, T/C cell excitation, conditioner temperature, and ullage temperature.

Accuracy of the analyzer is estimated to be within 0.3% parahydrogen (Appendix B).

Figure A-9 Data Acquisition System

A gas supply of 0.33 scfh is adequate for analysis. The essential details of the gas flow-control panel are visible in the analyzer photograph (Fig. A-6). Sample gas comes in from the viewer's left and reference gas comes in from the viewer's right. By manipulating the valves, sample and reference gases are selected for routing to the T/C cell, and sample supply rates to the cabinet are regulated. Bypass valves, on the viewers extreme left, permit maintenance of flow in the two sample lines that are not currently being analyzed.

Accessories to the analyzer are a normalizer and a calibration chamber. Both units perform the function of converting hydrogen to the equilibrium proportions at some temperature of interest.

A.4.1 Normalizer

The normalizer has two 7-cc chambers filled with nickel chips. When high parahydrogen is passed over the nickel at 1400°R, a catalytic action takes place that converts the hydrogen to the normal form. A 165-watt heater, high-temperature thermostat, and monitoring Fe-Cu thermocouple provide temperature control. The assembly is insulated with 4 in. of vermiculite and is housed in a steel case.

A.4.2 Calibration Chamber

The calibration chamber contains about 10 cc of high-activity hydrous ferric oxide catalyst. In use, the chamber is placed in selected bathes of boiling liquid having known temperatures. When high-purity hydrogen is passed over the catalyst at a low flow rate, the gas emerges at the equilibrium parahydrogen concentration corresponding to the temperature of the chamber. This gas, of known composition, is used for calibration and reference purposes.

A.5 Miscellaneous Instrumentation

A.5.1 Liquid-Level System

A liquid-level system was incorporated to continuously monitor and control the level of liquid hydrogen in each dewar. Each dewar is equipped with a probe having thermocouples and low-wattage resistors at various known spacings from the dewar lid. These probes can be seen in Figures A-2 and A-3.

The large resistance change experienced by the probe resistors upon submersion in liquid cryogen (in this case hydrogen, although the system works with nitrogen as well) is used to excite indicator-lamps on a panel. A lighted lamp indicates that the associated resistor is in liquid.

Figure A-10 shows two Liquid-Level Panels (LLP). Three such LLPs are part of the permanent Radiation Effects Testing System (RETS) installation.

A Bristol recorder-controller unit is used to regulate the cryogen. This unit is an electropneumatic device that translates the emf from the probe thermocouple into a proportional pneumatic signal. This signal is used to drive a pneumatic valve set in the dewar supply line at the cryogen manifold. A temperature record is also traced on a circular chart.

Seven sensor stations are used in the inner vessel probe. Spacing is such that there is a station at each 0.1 volume increment between the 0.9 and 0.3 volume levels, inclusive. Five stations are used in the outer dewar probe. Tables A-1 and A-2 show the arrangement of stations for the inner and outer probes, respectively.

A.5.2 Dewar Pressure

A 0.190-in.-i.d. pressure probe penetrating the ullage of each dewar leads to a transducer permanently located in the handling area. Dewar pressure is recorded by small strip-chart recorders mounted in the RETS console. An integral

Figure A-10 Liquid Level Panels

Table A-1

INNER-VESSEL LIQUID-LEVEL SENSOR SPACINGS

Station	Distance from Inner Dewar Lid ^a (in.)	Resistor	T/C	Fraction of Dewar Capacity
7	2 3/8	*	*	0.9
6	4 3/4	*		0.8
5	7 1/8	*	*	0.7
4	9 1/2	*		0.6
3	11 7/8	*	*	0.5
2	14 1/4	*		0.4
1	16 5/8	*		0.3

Table A-2

OUTER-VESSEL LIQUID-LEVEL SENSOR SPACINGS

Station	Distance from Outer Dewar Lid ^a (in.)	Resistor	T/C
5	20 1/2	*	
4	22 1/2	*	*
3	30		*
2	40	*	*
1	45	*	

^a Upper surface of inner dewar lid is 23½-in. from the outer dewar lid.

alarm system is set for 5 psig in the outer dewar and 10 psig in the inner dewar. Exceeding the alarm level not only results in a visible and audible alarm, but terminates cryogen flow by de-exciting the normally closed pneumatic valve which regulates the supply of the affected dewar. There is no override; cryogen flow cannot be reinitiated until the overpressure condition is relieved.

A.5.3 Explosive Mixture Detection

A 15-channel General Monitor (GM) explosive mixture detection system, modified by GDFWD for radiation-effects application, is a part of the permanent installation. The sensor heads contain part of a bridge, the elements of which are in contact with a hydrogen-sensitive catalyst-coated surface. When hydrogen contacts the catalytic surface, the heat of reaction increases the element temperature and thereby causes an unbalanced bridge condition which is registered by panel meters. A visual and audible alarm system is calibrated to trigger at 10% of the lower explosive limit (LEL) of hydrogen-air mixtures.

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APPENDIX B

ERROR ANALYSIS FOR THE PARA-
ORTHOHYDROGEN GAS ANALYZER

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APPENDIX B

ERROR ANALYSIS FOR THE PARA-ORTHOHYDROGEN GAS ANALYZER

There are two main sources of possible error in the gas analyzer: (1) instrumentation, and (2) measurement conditions. Each is discussed in detail below.

B.1 Instrumentation

Current Variations Due to Power Supply Voltage. The power supply used is the Gow-Mac Instrument Co. Model 40-05. Its stability over an 8-h period is better than 5 mV. Experiment shows there is less than 0.67% error in the measurement of parahydrogen when the current into the bridge changes by 1 mA. A 5-mV change in power-supply voltage corresponds to a bridge current change of 0.055 mA. By careful adjustment of the power-supply voltage prior to its use, the stability can be made much less than 5 mV. But accepting 5 mV as a worst case, the corresponding total error in the parahydrogen measurement is 0.037%.

Current Variation Due to Load Resistance. The normal current flowing into the bridge for equilibrium conditions is 300 mA. For a full-scale change in output, using the circuit of Figure A-7 (Appendix A), the current changes to 299.8 mA, or a change of 0.2 mA. This corresponds to a total worst case error of 0.13% in the parahydrogen measurement.

Digital Voltmeter Accuracy. The voltmeter used is the Dana Digital Voltmeter Model 5100. It has an accuracy of $\pm 0.01\%$ of reading or ± 1 digit, whichever is greater. Since full-scale output of the cell is in the neighborhood of 20 mV, and the voltmeter is a five-digit meter, the maximum error due to the voltmeter itself is 0.002 mV, which corresponds to a parahydrogen reading error of 0.0074%.

Printer. The accuracy of the printer is identical to the input device used. That is, the printer contributes no error to the system.

Test-Cell Repeatability. The thermal-conductivity cell used is the Gow-Mac Model 945430-S, which uses four tungsten elements as four legs of a Wheatstone bridge. The repeatability of the cell is absolute, with no error being contributed to the system by it.

Contact Resistance Throughout the Circuit. Assume that the maximum change in contact resistance throughout the circuit is 0.05 ohm. This is more than is actually obtained, as all connections are soldered, but using this as the worst case, the error in the parahydrogen reading due to contact resistance change is 0.1%.

B.2 Experimental Setup

T/C Cell Temperature. An experiment with a similar analyzer shows that the error due to 1°C (1.8°R) change in

cell block temperature is equivalent to a 5% parahydrogen error. The T/C cell in this experiment was immersed in an ice bath carefully regulated so that the temperature variation did not exceed 0.05°C (0.09°R). This corresponds to a parahydrogen error of 0.25%.

T/C Cell Pressure. Reference 7 indicates a 1% error in reading for a change of 40 mm-Hg in the cell pressure. The cell pressure was regulated to 1 mm-Hg in this experiment, so the contributing error is 0.025%.

Gas Flow Rate. Reference 1 shows that a change by a factor of 10 to 20 in the flow rate of either the sample or unknown gas through the cell block gives an error of 1% in the parahydrogen reading. The flow rate is easily held to a worst case factor of 2, so that the contributing error is no more than 0.075%.

B.3 Maximum Total Error

Using the square root of the sum of the squares to determine the error due to the combination of the preceding causes, the total error expected is

$$\begin{aligned}\text{Max. Total Error} &= (0.37)^2 + (0.13)^2 + (0.0074)^2 + (0.1)^2 + \\ &\quad (0.25)^2 + (0.025)^2 + (0.075)^2 \\ &= 0.3\%\end{aligned}$$

Since worst cases were chosen, the minimum accuracy of the analyzer is $\pm 0.3\%$.

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APPENDIX C

GTR RADIATION EFFECTS TESTING FACILITY

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APPENDIX C

GTR RADIATION EFFECTS TESTING FACILITY

The GTR Radiation Effects Testing Facility is located in the Reactor Operations Area at the north end of the NARF complex. Figure C-1 is a plan view of the facility. Figure C-2 is a cutaway view of the irradiation test cell and the reactor tank. Figure C-3 is a top view of the same. During operation the reactor is moved into the closet-like structure built into the north wall of the GTR tank. Items to be irradiated are located near the bottom of the test cell at the north, east, or west sides of the closet, as indicated in the figures.

The reactor closet is constructed of 1-in.-thick aluminum plate and is partially covered by 1/4-in.-thick boral to attenuate thermal neutrons. The boral extends 36 in. east and west from the closet along the tank wall and 36 in. up and down from the horizontal centerline of the reactor core. The centerline is 57 in. above the test-cell floor.

The Ground Test Reactor is a heterogeneous, highly enriched, thermal reactor that utilizes water as neutron moderator and reflector, as radiation shielding, and as coolant. Maximum power generation is 10 MW. The GTR, in an aluminum enclosure to facilitate cooling-water flow, is suspended by an open framework that is carried on a horizontal positioning mechanism at

Figure C-1 GTR Radiation Effects Testing Facility

Figure C-2 GTR Tank and Irradiation Test Cell - Cutaway View

Figure C-3 GTR Tank and Irradiation Test Cell - Top View

the top of the reactor tank. This mechanism permits the reactor to be positioned at distances ranging from 2 to 87 in. from the north face of the closet.

Adjacent to the north wall of the irradiation cell is the handling area. In this area, various connections are made for cryogenic, hydraulic, and pneumatic equipment.

An integral part of the GTR testing facility is the shuttle system, which is used to move test assemblies into irradiation position. This system consists of cable-driven dollies mounted on three sets of parallel tracks. The tracks extend from the irradiation positions adjacent to the reactor closet, up an incline to the north wall of the irradiation cell, and to a loading area on the ramp just north of the handling area. The system can be operated from either the control room or the dolly motor-drive shed on the north ramp. Test setups that are incompatible with the shuttle system are positioned by means of an overhead crane.

The control room (see Fig. C-1) is a below-grade, reinforced-concrete structure adjacent to the GTR facility. The room provides a shielded area for reactor instrumentation, control consoles, and test systems, as well as special test equipment needed to conduct radiation experiments. Full-coverage tele-viewing of the irradiation cell, entire shuttle system, and

general outside area is provided in the control room by means of closed-circuit television.

More detailed information on the facility can be found in Reference 15.

APPENDIX D

CALORIMETRIC DETECTION OF LH_2 FREE RADICALS

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APPENDIX D

CALORIMETRIC DETECTION OF LH_2 FREE RADICALS

D-1. Free Radical Experiment

The assumption that the irradiation of liquid hydrogen produces H_3 molecules that are stable (or quasistable) in the liquid and highly dissociative in the gas is based on the results of a calorimetric experiment attached to a cryogenic insulation test performed at GDFWD during 1967. A detailed description of the experiment and analysis has been written for inclusion in the Cube B report (Ref. 7). Aluminum and quartz tubes of identical dimensions were mounted vertically on an insulative rod inside the Cube B dewar. The tubes were closed at the bottom and open at the top so that they would fill when the LH_2 level in the cube was raised and would retain LH_2 when the level was dropped slightly below the tops. The tubes were 12 in. long and had an inside diameter of 0.5 in. Inside each tube were three 1-k Ω resistors spaced 1 in. apart, each supported in a horizontal position by its lead wires. Each test resistor was in series with an external 6.6-k Ω resistor and a regulated 10-V power supply.

The voltage drop across each resistor was monitored on a Dymec recorder, with the GTR at either 0 MW or 3 MW. At 3 MW, the dose rate at the position of the tubes was 0.6×10^9 ergs/g(C)-h.

When the liquid level in Cube B was allowed to drop, the emergence of a given test resistor in the tube LH_2 was signaled by an emergence-signature in the voltage data. The rate at which the liquid boiled out of each tube was given by the time between emergence signatures. The temperature of the gas over the LH_2 was found by converting voltage to resistance and referring to a resistivity-temperature chart.

The original object of the experiment was to determine if, as a result of the absorption of energy from the wall-recombination of radiation-induced LH_2 free radicals, the LH_2 boiled out of the metal tube more rapidly than out of the quartz tube. Radicals such as atomic hydrogen often undergo surface recombination even when volumetric three-body recombination is frozen out by the existence of an activation energy for recombination. It was reasoned that if radiation-induced free radicals in LH_2 survived long enough to reach the wall of a propellant tank, a significant amount of localized heating could result from the transmission of recombination energy to the tank wall. In the Cube B experiment, a quartz tube was used as a reference, since, at normal temperatures at least, the H-atom recombination coefficient of quartz is orders of magnitude less than that of the Al_2O_3 layer constituting the surface of the aluminum tube and the walls of propellant tanks.

D-2. Results of the Experiment

The results of the experiment were:

- Heating of the aluminum tube was not significantly greater than that of the quartz tube; the heating of both was roughly equivalent to the nuclear-energy deposition.
- At 3 MW the rate of boiling in both tubes increased by about 10% over a continuous 4.6-h exposure.
- At 3 MW the temperature of the gas 1 in. above the liquid surface increased by about 0.7°K over a 4.6-h exposure; after reactor shutdown and retraction, the temperature of the gas 1 in. above the surface decreased with a time constant of roughly 6 h.
- Both the rate of boiling increase and rate of temperature rise in the gas just over the LH_2 surface appeared to obey the law of population growth with a time constant of roughly 3 h.
- An extensive analysis of various possible heat leaks and dose-rate increases showed that neither kind of effect could account for the increasing heating rates.
- Heat-transfer calculations showed that the increasing 3-MW boiloff was about what would be expected from the increasing gas temperature, so that gas heating due to some intrinsic source was the independent variable.

In accordance with the above findings, interest shifted from surface recombination to effects due to long-lived free radicals.

D-3. Proposed Explanation of Experimental Data

The simplest explanation of the above results is as follows:

- About 7.7% of the energy deposited by radiation in LH_2 is stored in the production of radicals that are stable in the liquid and that disappear rapidly in the gas phase, thereby producing exothermic reactions. The

lifetime of such radicals in the liquid is equal to $1/0.37$ of the average time that an H_2 molecule resides in the liquid before it is vaporized. The radicals are H_3 complexes formed with a production factor of 3.3 molecules/100 eV. (If this explanation is quantitatively correct, radiation-induced free-radical production is not likely to be important from the standpoint of direct LH_2 heating in aerospace applications, but could be quite significant from the standpoint of $p-H_2$ conversion at elevated temperatures.)

D-4. Agreement of Theory and Experiments

The quantitative consistency of the above explanation with the gas-phase temperature data is shown by comparing the gas heating over the liquid, inferred from the observed temperature rise, with a population growth law in which the parameters are chosen for best agreement. The temperature rises for resistor 2 are shown in Figure D-1 along with an arbitrary smooth fit to the data. It was hypothesized that free radicals were produced in the liquid which are stable in the liquid but which decompose rapidly in the gas, producing an amount of heating per unit surface area of liquid designated as $\dot{h}_l$. The points in Figure D-2 represent the intrinsic heating, $\dot{h}_l$, inferred from the observed temperature increases (Fig. D-1) and the specific heat of gaseous hydrogen, C_p :

$$\dot{h}_l(t) = \dot{B} C_p(T - T_1) \quad (D-1)$$

where $\dot{B}$ (g/cm^2 -sec) is the rate of boiloff per unit area at 3 MW, T is the observed gas temperature at time t , and T_1 is the temperature of liquid hydrogen.

Figure D-1 FRT Resistor-2 Temperature in Gas Phase - Continuous 3-MW Reactor Power

If the free-radical production rate is P_r (radicals/cm³-h) and if the free-radical concentration in a continuously replenished dewar, n (radicals/cm³), is limited only by the vaporization of the radicals, then the concentration at a time t after reactor startup is given by

$$n = \frac{P_r}{f} (1 - e^{-f\dot{\beta}t}) \quad (D-2)$$

where $\dot{\beta}$ is the fractional boiloff rate of LH₂ in the dewar and f is the relative fugacity of the radicals (probability of being vaporized relative to that of H₂ molecules). If the potential energy represented by each radical in the liquid is E and the density of the liquid is ρ , the rate of intrinsic heating per unit area corresponding to Equation D-2 is

$$\dot{h}_i(t) = E \left(\frac{\dot{\beta}}{\rho} \right) f n = E h P_r (1 - e^{-f\dot{\beta}t}) \quad (D-3)$$

where h is the height of the LH₂ volume. In the case of Cube B

$$h = 75 \text{ cm}$$

$$\dot{\beta}(3 \text{ MW}) = 0.93 \text{ h}^{-1}$$

Figure D-2 shows the comparison between the observed gas temperature, transformed by Equation D-1, and the evaluation of Equation D-3, where P_r and f are chosen to be

$$P_r = 3.38 \times 10^{18} \text{ radicals/cm}^3\text{-h}$$

$$f = 0.3729$$

Figure D-2 Intrinsic Heating of GH₂ at 3-MW Reactor Power - Temperature Data

It is also assumed that E is equal to one-half of the H_2 dissociation energy:

$$E = 3.8 \times 10^{-19} \text{ joule}$$

A deliberate discrimination has been made against the Run 6 point, since Run 6 represented a last-minute effort that was started just before reactor shutdown at a time when the thermal transients associated with Run 5 had not disappeared. The fit to the other four points is seen to be reasonably good.

The boiloff rates were obtained from the time between emergence signatures of the resistors in each tube and are therefore independent of the temperature data. Figure D-3 gives the power into the quartz tube inferred from the boiloff rates and the vaporization heat of LH_2 . Since the boiloff increases are attributable to heat transfer from the warming gas, the comparison with the growth law is made in Figure D-4 by normalizing to the Run 5 value of $\dot{h}_i(t)$ in Figure D-2. It is seen that, except for the Run 6 result, the boiloff data are in accord with the data on gas temperature. The time constant $1/f\dot{\beta} = 2.9 \text{ h}$, corrected for the reduced rate of boiloff at 0 MW, is found to give a reasonable description of the observed gradual decrease in gas temperature after shutdown. It is therefore evident that both the temperature and boiloff data at 3 MW and the temperature data of 0 MW (where no boiloff data were obtained) can be

Figure D-3 Power into Liquid in Quartz Tube - Continuous 3-MW Reactor Power

Figure D-4 Intrinsic Heating of GH₂ at 3-MW Reactor Power - Boiloff Data

correlated quantitatively on the assumption that radiation produces energy-storing free radicals that are stable in the liquid and highly dissociative in the gas.

D-5. Energy-Storage, Fugacity, and Probable Energy-Storing Species

The fraction of deposited energy that is stored in the form of free radicals can be estimated from the asymptotic value of $\dot{h}_i(t)$ given by Equation D-3 and the total rate of 3-MW energy deposition by radiation in the cube. The latter was determined from boiloff rates to be 1949 watts. The result is that 7.7% of the energy is stored, which corresponds to a production factor of

$$G = 3.3 \text{ radicals/100 eV}$$

if it is assumed that the formation of a pair of radicals stores an amount of energy equal to the H_2 dissociation energy. Although a 7.7% storage of radiation energy is too small to be noticeable as an initial energy sink in reactor experiments, it is quite high in terms of the low radical concentrations required for catalysis of conversion.

The fact that the inferred relative fugacity of the free radicals, $f = 0.37$, is less than unity shows that the stable radicals are not free H atoms and are, in fact, more massive than H_2 molecules. This result is quite reasonable. A recombination rate calculation has been made which indicates that even

if H_2 molecules were ineligible as third bodies, the rate of H-atom recombination in the liquid with other H atoms as third bodies would be far too high to permit the concentration indicated by Equation D-2 for a 3-MW run time of 4 h, viz.,

$$n (4 \text{ h at } 3 \text{ MW}) = 7.3 \times 10^{18} \text{ radicals/cm}^3$$

Since previous experiments have indicated that the ions produced by radiation in liquid hydrogen disappear rapidly (Ref. 4), it follows that the stable radicals must be "hydrated" H atoms, or complexes formed by an H atom and one or more H_2 molecules. The simplest such complex and the only one whose properties are known well enough to permit a discussion of its possible amenability to stabilization is the linear triatomic configuration H_3 .

D-6. Formation and Stabilization of the H_3 Complex in LH_2

The symmetric H_3 complex has been well studied because of its role in the conversion of one hydrogen modification to another at elevated temperatures. The potential-energy contours for an H atom approaching an H_2 molecule prior to the formation of such a complex have been derived by Hirschfelder et al. (Ref.16) using a quasi-quantum mechanical model. A cross section of the resulting potential field in real space is shown in Figure D-5. The same H_3 potential-energy contours in configuration space are shown in Figure D-6 along with a possible system-points trajectory. It is seen that for an H atom to cross the threshold

$$1 \text{ kcal/mole} = 0.0434 \text{ eV/molecule}$$

Figure D-5 Potential-Energy Contours for an H Atom Approaching an H₂ Molecule

1 kcal/mole = 0.0434 eV/molecule

Figure D-6 H₃ Potential-Energy Contours and Representative System-Point Trajectory in Configuration Space

leading to the potential energy "crater" at one end of the H_2 molecule requires a relative kinetic energy of about 7 kcal/mole (0.3 eV). It is therefore impossible for an H atom that is "thermalized" in liquid hydrogen to form even a transitory complex of the type indicated by Figures D-5 and D-6.

The identification of the stable free radical produced by radiation in LH_2 with the H_3 complex is based upon two alternative possibilities. One is that since H atoms produced by ion neutralization have initial kinetic energies on the order of 3 or 4 eV, such an atom may have several chances of surmounting the potential barrier and forming a complex that could become quasi-stable by subsequent energy transfer to surrounding molecules. However, no data are available on the lifetimes of such quasi-stable complexes. A more likely possibility is the formation of a weakly bound but truly stable complex of a form not indicated by Hirschfelder potential contours.

In 1957 a calculation of the $H-H_2$ potential-energy surface was made by Lippincott and Leifer (Ref. 17) which indicated the existence of a linear asymmetric H_3 configuration that is (classically) stable by 1.43 kcal/mole and that is formed with no activation energy. The potential-energy minimum corresponds to an H-atom position that is $2.06 \overset{O}{\text{\AA}}$ from the nearest of a pair of H-atoms separated by $0.769 \overset{O}{\text{\AA}}$ (see Figure D-7). Lippincott and Leifer noted that the inferred stable H_3 molecule was in some

Figure D-7 H_3 Potential-Energy Surface of Lippencott and Leifer Showing Potential Minima and Lowest Point on Barrier to Symmetric Complex Formation

respects similar to the stable N_3 configuration that has been observed at low temperature and suggested an infrared spectroscopic experiment to detect H_3 . The fact that their calculations led to one of the better predictions of the activation energy for conversion (6.8 kcal/mole) gives support to the assumption that seems to be required by the calorimetric experiment, viz., that a loosely bound but stable H_3 configuration is readily formed by $H-H_2$ association in which the energy of formation is absorbed by nearest neighbors in liquid hydrogen. Such a process would compete with H-atom recombination and, since the activation energy for reactions such as

should be at least 2(1.43) kcal, the H_3 complexes would be unlikely to disappear by homogeneous recombination at liquid-hydrogen temperature.

Once the H_3 complex is stable and thermalized in the liquid, it is quite possible that the vibratory motions of neighboring molecules cannot deform the H_3 potential sufficiently to induce dissociation of the quasi-stable complex. This assertion is based on the idea that the individual particle modes in the liquid are vibrations that are of sufficiently low energy to be constrained by attractive rather than repulsive forces and that the higher energy modes are collective. Since the long-range attractive

forces should not be able to deform the H_3 potential contours, and since the energy of the high-energy modes is distributed over a number of molecules that vibrate cooperatively, no strong short-range repulsive forces should be exerted on the H_3 complex. It is therefore reasonable to suppose that in the liquid a quasi-stable H_3 complex will not acquire enough energy either to dissociate or to undergo homogeneous reactions with other H_3 molecules.

On the other hand, in hydrogen gas at LH_2 temperature and atmospheric pressure an H_3 complex would experience about 10^{10} repulsive collisions per second. If only one in 10^7 of such collisions perturbed the complex enough to disintegrate it, the gas-phase temperature rise observed in the experiment would be explained. The H_3 complexes would decompose to H atoms and H_2 molecules within 10^{-3} sec (the time required for the H_2 gas to rise about 0.001 cm in the Cube B experiment) and the H atoms would start to recombine with H_2 molecules as third bodies.

Although it has not shown quantitatively that H_3 can be formed with a G-value as high as 3.3, that the resulting complexes are stabilized in the liquid, or that they dissociate rapidly in the gas, the above discussion shows that the hypothesis of radiation-induced H_3 molecules that are stable in the liquid and highly dissociative in the gas is inherently plausible and in accord with all of the calorimetric data. It therefore

seems reasonable to use the H_3 complex model and the above values of f and P_r for the interpretation of the conversion data.

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