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The Conversion of Para to Orthohydrogen in a Gamma-Ray and Neutron Radiation Field

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THE CONVERSION OF PARA TO ORTHOHYDROGEN IN A GAMMA-RAY AND NEUTRON RADIATION FIELD

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ABSTRACT

The radiation induced conversion of para to orthohydrogen was investigated at pressures between 150 and 2200 psig (1 to 15×10^6 N/meter²) at three temperatures: 77 K (LN₂), 200 K (dry ice) and 300 K (ambient). Two radiation dose levels were studied: gamma rays only at 8×10^6 rads and a combination of 5×10^{14} n/cm², $E > 1$ MeV, plus gamma rays at 8×10^5 rads. The conversion at LN₂ temperature was nearly zero in all cases.

I. INTRODUCTION

Hydrogen is a mixture of two molecular species: orthohydrogen (parallel nuclear spins) and parahydrogen (antiparallel nuclear spins). The equilibrium composition varies with temperature from essentially all parahydrogen at liquid temperature (20 K) to "normal" hydrogen (25% parahydrogen) at room temperature or greater. In the absence of catalysts, conversion to equilibrium upon temperature change is quite slow (days).

The nuclear rocket uses hydrogen as the propellant. The entering liquid hydrogen first flows through the nozzle coolant passages for regenerative cooling, then provides cooling for a beryllium neutron reflector. The hydrogen now gaseous at approximately 110 K and 1000 psig enters the turbine portion of the turbopump, the energy being provided for the drive by the enthalpy gain of the hydrogen in the nozzle and reflector. (The pump end of the turbopump in turn pumps the liquid hydrogen from the tank into the nozzle.) The hydrogen discharged from the turbine enters an inlet plenum and flows directly through small channels in the reactor core where typically the temperature rises to 2500 K. The hot hydrogen gas

is then expanded through a nozzle to provide thrust at very high specific impulse (> 800 seconds).

Because the design for the turbopump was based on the thermal properties of parahydrogen and because the enthalpy of orthohydrogen is smaller than that of parahydrogen conversion to equilibrium, concentration could result in a pump drive energy deficit of as much as 21%. In passing through the high temperature core region complete conversion to normal hydrogen occurs, but this is downstream of the turbine drive and furthermore at these temperatures the properties of para and normal hydrogen are not different.

Experiments with parahydrogen flowing through similar materials and at similar temperatures as those encountered in the nozzle and reflector regions showed no conversion. Thus for design purposes the assumption of parahydrogen properties seemed justified. However, experiments using the Phoebus 2A and *Probe 1* reactors in 1968 indicated that conversion towards equilibrium hydrogen did occur in the nozzle-reflector region where intense radiation fields existed during reactor operation.

Although these experiments were not sufficiently clear cut to provide definite proof that the conversion would take place in the existing time scale and at the existing dose levels, they did show that additional information should be obtained. Therefore, experiments were designed on a laboratory scale to show whether the above mentioned conversion was due to radiation or some systematic cause in the sampling technique. Theoretical calculations indicated that no appreciable conversion would take place.

The experiments discussed below were therefore designed with the following objectives in mind.

1. To determine how much conversion takes place under temperature, pressure and radiation conditions which exist in the NERVA nozzle, reflector, and turbine.
2. To determine additional conversion data at higher temperatures and lower pressures where possible.
3. To shed light on the radiation induced mechanism.

Previous progress reports have been made both verbally and by letter. This report constitutes the final report of this project, R-065 (SNSO Contract Number SNC-97).

II. EQUIPMENT

A. Liquid to Gaseous Hydrogen Converter

The parahydrogen samples were taken from a liquid to gaseous hydrogen converter (LH_2 to GH_2) at the Los Alamos Scientific Laboratory. The hydrogen is stored as a liquid in a 14,000 gallon dewar and the liquid, as sampled, has a parahydrogen concentration greater than 95%. The sample canisters for irradiation were filled on the high pressure side of the converter at pressures up to 2200 psig at ambient temperature.

B. Sample Canisters

1. Single Sample Canisters. The sample test canisters for most of the irradiations were especially designed for this program and were made from 20-mm diameter brass hex bar stock 55-mm long. A 3-cm³ hole was drilled into the brass and the hollow hex tube was then welded to a brass needle valve. The canisters were pressure tested to 5000 psig and cycled between ambient and liquid

nitrogen temperatures several times. They were also tested for catalytic inertness by storing parahydrogen in them for 72 hours with periodic analyses of parahydrogen concentration to demonstrate that they did not convert the parahydrogen to orthohydrogen at a rate greater than expected by the uncatalyzed thermal processes.

2. Four Sample Canisters (Four-Holer). A special canister was designed and built to satisfy the safety requirements for operation in the Sandia Annular Core Pulse Reactor. The most difficult requirement to meet was the use of liquid nitrogen (LN_2) with a maximum oxygen impurity of 10 ppm (by volume).

A cylindrical copper block 75-mm in diameter and 75-mm high had four 3-cm³ holes drilled in it at constant radius. Needle valves were welded into these holes. A helical groove was machined around the block and a copper tube was soldered into this groove and connected so that LN_2 could flow around the block to cool it. Four thermocouples were soldered into the block at various elevations; two at the same elevation as the center of the sample holes, one above center and one below center; all at the same radius as the sample holes. A brass can was welded outside of the block leaving a 1-in. annular vacuum space around the block. The can was coated with a 1-in. layer of closed pore polyurethane foam. The LN_2 inlet tube was attached to an insulated 3/8-in. diameter corrugated stainless steel line 30-ft long which in turn was attached to a pressurized 50-liter LN_2 dewar. The exit line was fitted to a 30-ft 1/2-in. diameter corrugated (uninsulated) line which was attached to a vent line above the reactor.

3. Other Canisters. Several aluminum canisters were made similar to the brass canisters discussed in section B-1 above. Also a stainless steel canister was made to determine whether this paramagnetic material would catalyze the conversion of para to orthohydrogen.

Two brass canisters like those described in section B-1 were filled with beryllium and Inconel-718 chips, respectively, in order to determine whether or not these materials would catalyze the conversion.

C. Annular Core Pulse Reactor

After several initial irradiation tests were

made using the Godiva and Jezebel reactors at LASL and the SPR-II reactor at Sandia, all of the subsequent neutron irradiations were made with the Sandia Annular Core Pulse Reactor (ACPR).⁽¹⁾ Most of the irradiations were 6-msec half-width pulses giving 1.5×10^{15} n/cm², $E > 10$ keV (this value is equivalent to 5×10^{14} n/cm², $E > 1$ MeV for the ACPR spectrum) and 1.6×10^6 rads (H₂). A few steady-state irradiations were run at the same integrated flux and dose. These irradiations lasted 300 seconds.

D. Gamma Irradiation Facility

The gamma irradiations were done in the 130,000 curie cobalt Gamma Irradiation Facility (GIF) at Sandia.⁽²⁾ The maximum test dose desired was 1.6×10^7 rads (H₂) which took 90 minutes to obtain.

E. Analytical Apparatus

The concentration of orthohydrogen in parahydrogen determination was based on the differences in their thermal conductivities. A double thermal conductivity cell bridge circuit was used. Normal hydrogen (75% ortho and 25% para) was used as the reference in one cell. Due to its higher thermal conductivity the greater ability of parahydrogen to remove heat from the resistance wire in the cell changes the temperature of the wire thus changing its resistance and the potential drop across the wire as a function of parahydrogen concentration.

A Beckmann GC-2A gas chromatograph was used to analyze the hydrogen gas for impurities.

III. EXPERIMENTAL PROCEDURE

A. Taking Samples

A nine position sample manifold fitted with a bourdon tube pressure gage and a thermocouple vacuum gage was attached to the high pressure side of the LH₂ to CH₂ converter. The manifold was alternatively flushed with the converter CH₂ discharge gas and pumped down to 1-2 microns several times before sampling. The experiments were performed at three densities: 1) full density (0.012 g/cm³, 2200 psig when filled at ambient temperature), 2) half density (0.006 g/cm³, 1100 psig when filled at ambient temperature), and 3) quarter density (0.003 g/cm³, 550 psig when filled at ambient temperature) except in a few

cases where these pressures could not be attained. In most cases the canisters attached to the manifold were filled to > 2200 psig and then bled down to the desired pressure. In some cases when the four holer was used, a 50-cm³ canister was used to transport gas between Los Alamos and Sandia and the gas was transferred to the test vessel at Sandia. When this was done, we were unable to attain the desired maximum pressure of 2200 psig, reaching a pressure of about 1700 psig instead. We later showed, however, that the effect of pressure is not statistically separable from other variables in our data.

B. ACPR Runs

1. Ambient Temperature. For the ambient temperature ACPR irradiations the samples were placed in a phenolic bucket and lowered into the core cavity. After the irradiation burst the temperature rose about 40°C to 70°C. Unirradiated control experiments indicated that this amount of heating for short periods of time had no effect on conversion. No coolant such as water could be permitted in the ACPR because of its effect on the reactivity of the reactor.

2. Dry Ice Temperature. The temperature of approximately 200 K was maintained during some irradiations by simply packing the canisters with crushed dry ice in the phenolic bucket. A 40 K temperature rise was noted after the irradiation burst but this quickly cooled back to the starting temperature and no effect on the conversion was detected.

3. Liquid Nitrogen Temperature. Because of numerous explosions in reactors at many different locations when LN₂ is put into reactors, strict precautions had to be taken.⁽³⁾ During prolonged irradiations using LN₂ which is exposed to air (O₂) and moisture, a green solid forms which upon warming can spontaneously detonate causing a potential hazard to equipment and personnel.

To preclude the possibility of an explosion, the LN₂ was kept within an entirely closed system from the supply dewar (helium pressurized) through the reactor dewar until the vaporized GN₂ passed through a flow meter, a check valve and out the vent stack. The transfer system was purged for several minutes through a by-pass before filling. The LN₂ in the 50-liter dewar was analyzed after

filling and immediately before use by an incandescent bulb oxygen analyzer which gave a positive identification when the LN_2 sample contained more than 4 ppm (by volume) oxygen. On occasion the O_2 content was verified by gas chromatography.

The four-holer canister described above (Section II-B-2) was the most frequently used. An earlier model used a vacuum jacketed vessel which was about 3/4 full of LN_2 . This system had the advantage of having the canisters immersed in LN_2 and assuring a temperature very close to 77 K (LN_2 boiling temperature). It, however, required a resistor level sensing system which proved unreliable in a radiation field.

The four-holer was completely satisfactory except that we were unable to attain temperatures below 87 K in the best case and 117 K in the worst. This, however, turned out to be an advantage because very little conversion was witnessed even at 117 K indicating that conversion did not take place at 117 K or below. This system was very difficult to work with because it remained very radioactive for several hours after the irradiation burst and the analysis had to be accomplished in that period. This required rapid transfer of the sample containers from the reactor to the analysis equipment and reading dials and gages with binoculars in order to minimize the radiation exposures of personnel. The results, however, were gratifying.

C. GIF Runs

Because of the long exposures required to attain the desired gamma dose in the GIF, the samples had to be cooled. The samples were placed in a stainless steel dewar and cooled with one of the following: 1) an ice-water mixture for "ambient" temperature, 2) a dry ice-acetone mixture, and 3) LN_2 .

IV. RESULTS

A. ACPR

The data from the ACPR are summarized in Table I. The full density data taken on samples that were filled to between 1700 and 2200 psig have been pooled for brevity. The data taken at temperatures between 77 K and 117 K were also pooled. The data in the low temperature range are shown in Table II. The conversion at the low

temperatures, 77-117 K, ranges between 0 and 2% indicating very little radiation effect. Appreciable conversion was found at 196 K and ambient temperature but the scatter of data was quite large.

B. GIF

The GIF data are summarized in Table III. For reasons to be discussed later, the ambient and dry ice temperature data show large standard deviation. The LN_2 data seem to agree well with the ACPR data, i.e., no conversion takes place at LN_2 temperatures.

C. Comparison of Burst Versus Steady-State Irradiations in the ACPR. (Rate Effect).

The data shown in Table IV indicate more conversion at constant fluence for a longer time than with the same total dose in a high flux burst.

D. Effect of Oxygen (Air) on Conversion of Unirradiated Parahydrogen

Table V shows that oxygen in the range of 0.2 ppm (by volume) can catalyze the conversion of parahydrogen to orthohydrogen. The detection limit of the oxygen by the routine gas chromatograph technique used was about 2 ppm (by volume). Consequently, the estimation of the oxygen concentration was inferred from the makeup ratios rather than from analyses.

E. Effect of Catalysts. Parahydrogen stored in a 304 stainless steel canister for 72 hours at ambient temperature and 2200 psig showed almost complete conversion to normal hydrogen (75% orthohydrogen and 25% parahydrogen). Similar samples stored for 72 hours in brass canisters converted from parahydrogen to a mixture of 27% orthohydrogen and 73% parahydrogen, indicating a smaller catalytic effect than that of the previously mentioned stainless steel canister.

Attempts were made to determine whether the materials that the hydrogen would flow through in the nuclear rocket would cause para to orthohydrogen conversion. Both irradiated and unirradiated samples of parahydrogen in the presence of beryllium and Inconel-718 gave inconclusive results. In some cases the unirradiated control samples showed more conversion than the irradiated samples in the presence of these materials.

V. DISCUSSIONS

Several mechanisms have been proposed for the radiation induced conversion of parahydrogen to orthohydrogen. The one that seems to fit the experimental data the best is the ion-molecule reaction of Thompson and Schaeffer:⁽⁴⁾

where the H_2 molecule can be either para or ortho-hydrogen. In our experiments care was taken to make sure that initially the H_2 was essentially pure parahydrogen. The H_2 molecule on the right is para or orthohydrogen based on the probability of formation at the particular temperature of the reaction. The equilibrium concentration at 20 K is nearly pure parahydrogen (99.8%). At room temperature and above the equilibrium concentration is 25% parahydrogen.

The third body, R, can be an H_2 molecule, the vessel wall or an impurity species such as oxygen. The third body must have the ability to absorb enough energy from the product species so that they will not fly apart and continue propagating the chain. If the third body is paramagnetic such as oxygen, it can play the dual role of ending the chain and converting the parahydrogen to ortho-hydrogen by a magnetic mechanism. Impurities can reduce the degree of conversion by reacting with a chain initiation species:

or by reacting with the chain propagation species:

Based on our experiment (see section IV-D and Table V) showing that subliminal amounts of air can catalyze the para to orthohydrogen conversion, it is not difficult to extrapolate this reasoning such that the same quantities of air or other impurities could inhibit the radiation induced chain initiation and chain propagation shown above. The conversion which takes place at room

temperature and above without ionizing radiation or catalysts present is thought to have a free radical mechanism where the free radical is the hydrogen atom. The rate determining step is dependent on the population of H atoms created by collisions:

A paramagnetic species such as oxygen would promote an alternate reaction by providing an inhomogeneous magnetic field as described by Farkas⁽⁵⁾ and Wigner.⁽⁶⁾

The presence of a paramagnetic impurity in our radiation induced experiments could give a falsely low conversion rate by consuming initiation and propagation species or a falsely high conversion rate by the magnetic mechanism. If the only impurity present is oxygen then one might expect the magnetic mechanism to predominate. If the sources of impurity are undetectable traces of air which leak into the system then there would be four molecules of nitrogen present for each oxygen molecule. The nitrogen molecules are capable of consuming initiation and propagation species by proton transfer but not capable of causing magnetic conversion because nitrogen is diamagnetic. The proton transfer mechanism is:

These arguments, though not confirmed, do give qualitative suggestions which could explain the large variances in the data, especially the GIF data where the ultimate dose of radiation was accumulated over a 90 minute period. Future experiments in this field should be accompanied by a more sensitive impurity assay technique than the technique sensitive to 2 ppm (by volume) which was used in these experiments.

The data given in Table IV indicate that a radiation dose applied over an extended period of low flux will cause a greater amount of conversion than the same dose delivered in a burst. Assuming the Thompson and Schaeffer mechanism above, this can be explained by the fact that the neutrons or

gammas that initiate the reaction by forming H_2^+ (which quickly reacts to form H_3^+) also form electrons in the same proportions. The H_3^+ concentration appears in the chain propagation as the first power, i.e., $H_3^+ + H_2 = H_3^+ + H_2$ and in the chain termination as the second power:

where H_3^+ concentration equals the e^- concentration. Increasing the gamma or neutron flux favors the chain termination step and inhibits the chain propagation.

VI. CONCLUSIONS

The extreme conditions of this study greatly complicate the carrying out of the experiment. The high pressures require heavy, thick walled containers and the low temperatures require insulated containers (dewars). The high radiation doses cause high activation of massive equipment and the combined reactor and industrial safety requirements greatly restrict experimental activities. In spite of these limitations most of the objectives of the experiments were fulfilled.

We have shown that:

1. Parahydrogen does not convert to orthohydrogen appreciably at nuclear rocket conditions of 5×10^{14} n/cm², $E > 1$ MeV, and 3×10^6 rads, 77-117 K at pressures between 550 and 2200 psig (ambient).

2. Conversion is readily catalyzed by paramagnetic substances such as stainless steel vessels and traces of oxygen.

3. There is a marked rate effect. Given equal doses of radiation, the low flux over a long period of time will cause more para-to ortho conversion than the high doses in a very short time.

4. Conversion at 196 K and 300 K was appreciable in both the reactor and the gamma irradiator. The data scatter was larger than expected.

Future experiments should include a very sensitive analysis technique such as chemiluminescence induced by the rare gas metastable energy transfer method. This technique can be used to detect 0.1 ppm (by volume) oxygen in the presence of hydrogen. Using this, and possibly other techniques, additional irradiated and unirradiated experiments as a function of trace impurities (approximately 0.1 ppm [by volume]) should be run. If this does not explain the spread of data at the higher temperatures, other causes should be sought. If the safety requirements can be satisfied, data should be gathered from flowing rather than static hydrogen in an effort to reduce the impurity and wall effects.

TABLE 1
RADIATION INDUCED PARA-TO-ORTHOHYDROGEN CONVERSION DATA FROM ACPR EXPERIMENTS

Temperature (K)	77 (LN ₂)			195 (Dry Ice)			300 (Ambient)		
Pressure (psig) ^a	550	1100	2200	550	1100	2200	550	1100	2200
Average ^b	0	0	1.0	25.9	15.8	17.3	25.8	35.3	32.0
Standard Deviation	---	---	0.7	3.8	7.6	8.3	5.4	10.9	5.7
Number of Samples	1	3	7	5	19	23	8	11	12

^aAt filling, before cooling from ambient temperature.

^bPercent orthohydrogen converted from parahydrogen by 5×10^{14} n/cm², $E > 1$ MeV plus 8.4×10^5 rad gamma.

TABLE II
RADIATION INDUCED PARA-TO-ORTHOHYDROGEN CONVERSION DATA FROM ACPR EXPERIMENTS
AT LOW TEMPERATURES ONLY ^b

Temperature (K)	Pressure (psig) ^a			
	550	1100	1700	2200
77	---	---	---	0
83	---	---	0	---
83	---	0	---	---
83	---	0	---	---
113	---	0	---	---
113	0	---	---	2.0
117	---	---	---	1.5
117	---	---	---	1.5
117	---	---	---	1.5
117	---	---	---	1.5

^aAt filling, before cooling from ambient temperature.

^bPercent orthohydrogen converted from parahydrogen by 5×10^{14} n/cm², E > 1 MeV plus 8.4×10^5 rad gamma.

TABLE III
RADIATION INDUCED PARA-TO-ORTHOHYDROGEN CONVERSION FROM GIF EXPERIMENTS

Temperature (K)	77 (LN ₂)			195 (Dry Ice)			273 (Ice Water)		
	550	1100	2200	550	1100	2200	550	1100	2200
Pressure (psig) ^a	550	1100	2200	550	1100	2200	550	1100	2200
Average ^b	No Data	0.5	0.14	68.6	60.2	41.5	67.2	67.5	51.9
Standard Deviation	---	0.7	0.24	4.6	13.7	14.6	1.3	4.5	14.9
Number of Samples	0	5	5	5	7	5	3	2	9

^aAt filling, before cooling from ambient temperature

^bPercent orthohydrogen converted from parahydrogen by a 8×10^6 rad gamma field

TABLE IV

STEADY-STATE VERSUS BURST EXPERIMENT CONVERSION OF PARAHYDROGEN TO ORTHOHYDROGEN

<u>Pressure (psig)</u>	<u>% Orthohydrogen^a</u>	
	<u>Burst (6 millisecond)</u>	<u>Steady-State (250 seconds)</u>
550	25.8	55.0
1100	35.3	66.0

^aConverted from 5×10^{14} n/cm², E > 1 MeV and 8×10^5 rads gamma at ambient temperature.

TABLE V

EFFECT OF TRACES OF OXYGEN (AIR) ON PARAHYDROGEN TO ORTHOHYDROGEN CONVERSION OF UNIRRADIATED PARAHYDROGEN AT AMBIENT TEMPERATURE AND 2200 PSIG IN 24 HOURS

<u>Air</u>		<u>Oxygen</u>	<u>% Orthohydrogen</u>
<u>Partial Pressure</u>	<u>ppm (by volume)</u>	<u>ppm (by volume)</u>	
0 Microns Hg	0	0	2.5
100 Microns Hg	0.9	0.2	4.0
200 Microns Hg	1.8	0.4	5.0
500 Microns Hg	4.5	0.9	6.5
12 psia	5450	1100	75% (complete)

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