Applications of ortho-para hydrogen catalyst

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Abstract. The underlying theory of hydrogen Ortho-Para conversion has long been known, but the specifics of non-linear heat of conversion from normal to para hydrogen have not been widely disseminated in the cryogenic literature. These factors are reviewed and thermally efficient applications in liquefiers and back conversion cooling systems are illustrated.

1. Keywords: Ortho, Para, Hydrogen, Catalyst
2. Background

Ortho and para forms of hydrogen were identified in 1907 along with newly developing quantum physics. In 1927, Dennison [1] was credited with relating Fermi-Dirac quantum statistics to the ortho and para spins of hydrogen molecules. Further investigations of hydrogen properties continued as a research topic. In 1946, the U. S. National Bureau of Standards (NBS) undertook a comprehensive program to bring together (and add to) the knowledge base of the thermal properties of the hydrogen isotopes. This effort was completed in November 1948 with the publication of NBS Research Paper RP 1932 [2]. RP 1932 was a compendium of the physics state of the art of the hydrogen isotopes and it included Table 12 listing "Ortho-para composition at equilibrium" as a function of temperature from 10 to 500 K. (A copy of most of this information is shown below in Table 1).

Although it was a landmark physics document, RP 1932 did not address applications. This is partly true because there weren't any cryogenic hydrogen activities outside the laboratory in the 1940's. Introduction of fusion weapons based on hydrogen isotopes changed things in 1949. Although the weapons focus was on deuterium, quantities of far cheaper liquid hydrogen were needed for testing and equipment development. NBS was selected to build a laboratory to create relevant technology and to produce liquid hydrogen for testing at a site provided by the people of Boulder, Colorado. Equipment for "the world's largest hydrogen liquefier" was designed and built by NBS staff in Washington, DC and installed in a building designed and built by the Denver firm Stearns-Roger Manufacturing Company. The plant began producing liquid hydrogen at the rate of over 300 liters per hour in March 1952.

The thermal impact of normal (74.928% Ortho, 25.072% Para) to para hydrogen conversion was immediately recognized and a program to identify and test a catalyst to accelerate ortho-para conversion in the liquefier was initiated. NBS personnel in Boulder and Washington, DC, scientists at Los Alamos Laboratory and a University of Colorado Chemical Engineering Professor worked on the problem. In late 1952, Dr. Ed Grilly at Los Alamos successfully tested a catalyst consisting of Chromic Oxide on Alumina. This catalyst was installed in the liquid receiver of the Boulder liquefier and it began producing high para product in March 1953.

Despite information that could have been gleaned from NBS RP 1932, the early catalytic normal to para converters were all located in the product liquid receivers. Gas phase conversion was incorporated in some later liquefiers but the common design basis was an assumption that the 500 kJ/Kg heat of conversion was linearly distributed over the equilibrium temperature range from 300 to the 20.27 K para hydrogen boiling temperature [3]. R. B. Scott's classic 1959 book [4] contains a table illustrating the non-linear thermal impact of converting ortho to para hydrogen but, due to a lack of awareness or emphasis, this table is not referenced in the text. The more recent (1981) and most comprehensive hydrogen source book, NBS Monograph 168 [5], contains both a table and plot of the heat of O-P conversion as a function of temperature without impact commentary. The data source is RP 1932. The Monograph 168 ortho para hydrogen conversion data has been confirmed by the Hydrogen Properties Group at Washington State University [6].
3. Useful Ortho-Para Hydrogen Data

Ortho and para hydrogen is defined by parallel and anti-parallel spins of the atoms as depicted in Figure 1.

![Ortho and Para Spin Diagram](image)

**Figure 1.** Hydrogen Ortho-Para spins.

Definitive O-P data is shown in Table 1. The first column lists the temperature range of interest. The equilibrium para content for temperatures from 300 down to 20 K are presented in the second column and the related cumulative heats of O-P conversion from normal to para are given in the third column.

| Temperature K | Equilibrium Para Percentage | Heat of Conversion Normal to Para kJ/kg |
|---------------|------------------------------|----------------------------------------|
| 20            | 99.821                       | 527.138                                |
| 30            | 97.021                       | 527.138                                |
| 40            | 88.727                       | 527.117                                |
| 50            | 77.054                       | 526.845                                |
| 60            | 65.569                       | 525.531                                |
| 70            | 55.991                       | 521.770                                |
| 78            | 50.028                       | 515.500                                |
| 80            | 48.537                       | 513.932                                |
| 90            | 42.882                       | 500.757                                |
| 100           | 38.620                       | 481.671                                |
| 120           | 32.959                       | 427.248                                |
| 150           | 28.603                       | 322.495                                |
| 200           | 25.974                       | 163.774                                |
| 250           | 25.264                       | 70.524                                 |
| 300           | 25.072                       | 27.562                                 |

The cumulative heat of conversion from normal to para hydrogen is plotted in Figure 2 to illustrate the extreme non-linearity of the data. Figure 3 is plotted to focus on the cold end data and optimum location of conversion catalyst in a liquefier.
4. Analysis
As shown in Figure 2, the relation of O-P heat of conversion to temperature is significantly non-linear and impacts the thermal design of hydrogen liquefiers. The heat of conversion from normal to para is 500 kJ/kg in cooling from 300 K to liquid at 20.7 K. From 300 to 200 K the conversion heat removed is 27.27 % of the total,
from 200 to 100 K it is 63.63 % and only 9.1 remains to be removed to achieve 100 % para. Actually, any para percentage above 95 % is commercially acceptable. This is equivalent to the equilibrium para level at 90 K.

Examination of Figure 3 is particularly revealing. The heat of O-P conversion from 60 down to 20.7 K is only 1.607 kJ/kg or 0.32 % of the total. At a liquid nitrogen bath temperature of 78 K the total O-P conversion heat is 487.938 kJ/kg or 97.59 % of the total. It is clearly advantageous to concentrate the O-P catalyst in a bath cooled with liquid nitrogen.

Carnot work of cryogenic refrigeration is defined by \( W_c = (T_w - T_c) / T_c \). For \( T_w = 300 \) K, the Carnot work values are 2.85 W/W at 78 K and 13.8002 W/W at the 20.27 K boiling temperature of parahydrogen for a ratio of 4.8487. This is significant when one considers that 627.9 kJ/kg is required to cool hydrogen gas from 78 to 20.27 K and the latent heat is 445.5 kJ/kg for a total of 1073.4 kJ/kg. O-P conversion in the liquid receiver more than doubles the 20.27 K heat load to 945.5 kJ/kg.

5. Conclusions

1. O-P conversion is most efficient if done at approximately the 78 K temperature of liquid nitrogen.
2. No catalyst is needed in heat exchangers colder than 78 K but a small amount of catalyst should be installed in the liquid receiver to bring up the para content from 50% to over 97% at the thermal cost of 11.64 kJ/kg or 2.22% of the total.
3. Gas phase conversion in heat exchangers below 200 K can be effective but it is difficult to balance the heat exchangers with the extra heat load.
4. Back conversion cooling with catalyst is not useful below 90 K and is most effective in the range from 100 up to 200 K.

References

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