CONSTRUCTION OF A PARA-ORTHO HYDROGEN TEST CRYOSTAT

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ABSTRACT

In a prospective hydrogen economy it is necessary to verify the para concentration of the employed hydrogen. In case of a short storage time of about a few days only it has been shown that a partial conversion into para-hydrogen gives an optimized overall efficiency. Hence, an easy and reliable method of measuring the para-hydrogen concentration is needed.

In this paper, the concept and construction of a small test cryostat are described and first results are presented. The measuring principle is based on a catalytic induced adiabatic ortho-para conversion of a hydrogen gas flow starting from a known temperature. The operation of the system only requires a certain amount of liquid nitrogen as coolant. To determine the concentration of para-hydrogen it is only necessary to measure the temperature of the gas before and after the adiabatic catalyst cell. The measuring cryostat is used for further investigation of the spontaneous para-ortho conversion in the supercritical state. In addition, the design of the cryostat allows the investigation of different catalyst materials regarding the catalytic activity and possible degradation by using a known para concentration for the measurement.

KEYWORDS: hydrogen, ortho-para conversion, para ratio measurement

INTRODUCTION

The hydrogen molecule can exist in two different spin configurations: the so called ortho hydrogen and para hydrogen. Both configurations coexist with a ratio of ortho to para hydrogen depending on the temperature.

Hydrogen always strives for the lowest available energetic state, the so called equilibrium state. The ortho and para hydrogen concentration in this equilibrium hydrogen only depends on the temperature and is described by the Boltzmann
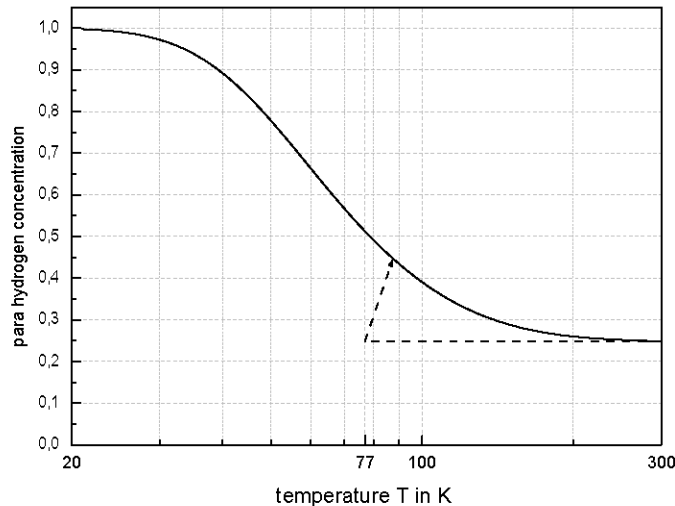
FIGURE 1. The Boltzmann distribution function showing the equilibrium para hydrogen concentration versus temperature. The dashed lines illustrate the temperature and concentration change of a normal hydrogen gas sample during a concentration measurement with fast cool-down from 300 K to 77 K and subsequent adiabatic catalyst-induced conversion.

distribution function [1]. This correlation can be seen in FIGURE 1. The conversion from ortho into para hydrogen plays an important role during hydrogen liquefaction and storage. The auto conversion has a time constant of several days [2]. The conversion can be enhanced by catalytic materials. In many cases hydrous ferric oxide [3] is used as catalyst.

The database for the characterization of this catalyst concerning correct dosage in a liquefier, regeneration procedure, poisoning and reactivity and is relatively poor. Furthermore its behavior with hydrogen at medium or high pressures hasn't been considered much in the past. The paper presents a measuring cryostat to determine the para hydrogen concentration of an unknown hydrogen probe. With this measurement device the described phenomena are planned to be partially investigated.

PARA HYDROGEN CONCENTRATION MEASUREMENT

General Measurement Techniques

To determine the para hydrogen concentration of an undefined hydrogen gas sample, every significant difference between the para and the ortho modification may be used. The main differences that are known and suitable for a measurement are

- the velocity of sound,
- the nuclear spin,
- the vapor pressure and
- the thermal conductivity.

The most common method used in the past was to measure the para hydrogen concentration by determination of the thermal conductivity. This method was first described nearly 80 years ago by Bonhoeffer and Harteck [4] and has been used widely. The main disadvantage of this method is the necessity of a reference measurement before each measurement of a probe [5]. For an industrial use there was the need for an

easier and more reliable method. This was found in measuring the heat of conversion and is still patented by the Linde AG [6, 7]. A device working on that principle was presented by Wanner in the year 1996 [7]. The measuring cryostat presented in the present paper might be seen as a further development of this earlier solution.

Measurement Using the Heat of Conversion

The measurement of the para hydrogen concentration is based on the enthalpy difference between ortho and para hydrogen. If the hydrogen is not in the equilibrium state and is converted by a catalyst into this lowest available energetic state the enthalpy difference leads to a temperature change of the hydrogen gas. This temperature change is unique for each para hydrogen concentration for a given starting temperature.

The basic thermodynamic working principle can be shown using the Boltzmann distribution in FIGURE 1. The dashed lines show this process as an example for a normal hydrogen probe with a para hydrogen concentration of 25 %. This gas sample is brought to a known temperature, e.g. 77 K by means of a liquid nitrogen bath. At this point the gas sample is not in an equilibrium condition. To measure the heat of conversion the gas sample is led through a nearly adiabatic catalyst filled passage and thus is converted into the equilibrium state. This catalyst filled passage is called the adiabatic conversion cell in the further description. At its outlet both gas temperature and pressure are measured. From the temperature at the outlet and the Boltzmann distribution function the concentrations of para hydrogen $x_{2,para}$ and ortho hydrogen $x_{2,ortho}$ can be deduced. The enthalpy h_2 at this point can be determined by equation (1)

$$h_2 = x_{2,ortho} \cdot h_{2,ortho} + x_{2,para} \cdot h_{2,para} \tag{1}$$

where h is the enthalpy, x is the concentration and the indices 1 and 2 means the inlet and the outlet of the adiabatic conversion cell. Considering the first law of thermodynamics the enthalpy change of the hydrogen gas during the conversation must be zero. Thus the enthalpy h_1 at the inlet must be equal to the enthalpy h_2 at the outlet. With the measured temperature and pressure at the inlet of the adiabatic conversion cell the initial para hydrogen concentration can be determined with equation (2) using an iteration method.

$$\frac{x_{1,para}}{x_{1,ortho}} = \frac{h_{1,ortho} - h_1}{h_1 - h_{1,para}} \tag{2}$$

EXPERIMENTAL SETUP

The basic components of the experimental setup can be seen on the right side in FIGURE 2. It consists of a double wall cryostat vessel with an LN2 bath, an immersed heat exchanger with a length of 7 m and a vacuum chamber with the adiabatic conversion cell thermally isolated inside. On the left side in FIGURE 2 the peripheral piping and valves can be seen with all necessary components.

The heat exchangers cools the hydrogen inlet flow down to nitrogen temperature with a maximum temperature difference of 0.1 K at its outlet. The calculated necessary length is only half of the actual length but this configuration provides the possibility to
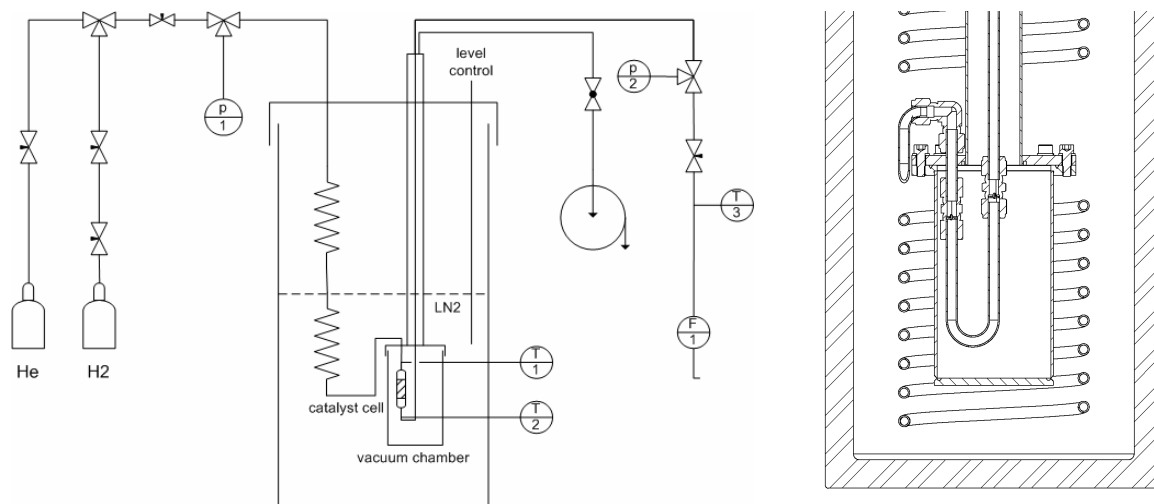
FIGURE 2. Left: Scheme of the measuring cryostat with peripheral piping and components. Right: Cross sectional view of the vacuum chamber with neck tube, spiral heat exchanger lines and an U-shape catalyst reservoir inside the LN2 bath cryostat.

use parts of the cold gas enthalpy of the nitrogen. Next, the 77 K gas in led through a U-shape tube filled with catalyst granulates inside the vacuum chamber. Right before the hydrogen enters the catalyst material the temperature is measured to ensure that the gas has nitrogen temperature. As catalyst material we use IONEX® type o-p catalyst material which is hydrous ferric oxide. The manufacturer suggests a specific flow rate of 1200 cm³ (STP) per minute per cm³ of catalyst [3]. With the specified flow rate the conversion is not complete, but at least suitable for a liquefier to ensure 95 % of para hydrogen. A closer investigation of this catalyst material was done in 1957 by Weitzel et al. at the National Bureau of Standards [8]. They showed that for a nearly complete conversion the specific flow rate should not be higher than 200 cm³ (STP) per minute per cm³ for this type of hydrous ferric oxide catalyst.

The main advantage of the presented measuring cryostat is the flexibility of the adiabatic conversion cell. It is possible to change the geometry and the catalyst material for analyzing purposes.

The first catalytic cell we use has a catalyst volume of 7 cm³. That leads to a maximum flow rate of 84 liters hydrogen per hour (STP) according to [8]. At the outlet of the adiabatic conversion cell the temperature is measured again and the original para concentration is calculated as described above.

The temperatures at the conversion cell are measured by Pt-100 temperature sensors inside the gas stream with a 4-wire measurement and a current of 1 mA. The measurement wires are placed inside the heat exchanger tubes and a warm electrical feed through is used outside the cryostat. The pressures are measured outside of the cryostat at ambient temperature. Actually, there are no capillary tubes to measure the pressure at the adiabatic conversion cell foreseen. Due to the low viscosity of hydrogen and the low volumetric flow, the pressure drop inside the heat exchangers is negligible.

The calculation of the para hydrogen content is based on the GASPAK properties database which refers to the hydrogen data from the NBS Report 168 [9]. A bug in the GASPAK Version 3.31 in the ortho hydrogen file could be fixed by R. D. McCarty in the near future [10].

FIRST RESULTS AND DISCUSSION

The experiments are being performed in the hydrogen test area in the cryogenic laboratory of the Technical University Dresden. In FIGURE 3 an experimental result from the commissioning phase can be seen. It shows the temperature change of normal hydrogen in the nearly adiabatic conversion cell.

The experiment starts with the cooling down of the whole system to liquid nitrogen temperatures. During this phase helium flows trough the heat exchangers and the conversion cell. After the complete cooling down it is switched to hydrogen supply. The measuring cryostat has two hydrogen inlets, one at ambient temperatures and one cryogenic inlet. If normal hydrogen is used, the outlet temperature of the conversion cell rises until a steady state is arrived. In FIGURE 3, three curves can be seen. The solid line represents the inlet temperature of the adiabatic conversion cell. The dashed line is the outlet temperature of the conversion cell. It rises from 77.6 K to 88.3 K. The dotted line represents the calculated temperature of 90.6 K for this test case with normal hydrogen which has a para concentration of about 25 %. This expected temperature is calculated with an iteration method using the Boltzmann distribution function and equations (1) and (2). The deviation from the first experimental results is 2.3 K. Reasons for this could be partly systematic errors due to heat conduction or on pre-conversion caused by any catalytic active impurities or surfaces in the heat exchangers. Further investigation will be done on this. The flow rate during the whole measurement was 83.4 liter per hour (STP) which is close to the design point of the conversion cell. The response time is relatively slow for a para hydrogen concentration measurement. It takes 30 min until $t_{0.9}$ is reached and another 30 min to achieve steady state. This corresponds roughly to the relative small hydrogen mass flow and the thermal masses of the conversion cell.
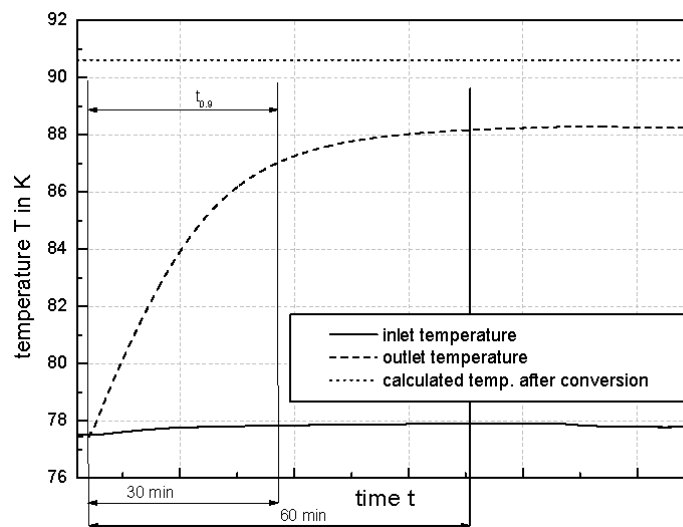

FIGURE 3. Experimental results during commissioning of the measurement cryostat.

The regeneration of the catalyst material during commissioning phase was realized with nitrogen and not with hydrogen as it is suggested [4]. Optimization of the volumetric design of the adiabatic conversion cell and investigation of catalyst regeneration effects are planned for the future. Further improvements to reduce residual heat leak are in progress. The estimated accuracy at the end is 1 to 2 % of para hydrogen concentration.

CONCLUSION

It has been shown, that a simple para hydrogen concentration measuring device with an easily exchangeable adiabatic conversion cell and cold vacuum seals can be built using the heat of conversion to determine the para hydrogen. The first results are promising that with some improvements and operational experience an accuracy of 1 to 2 % of para hydrogen concentration is realistic.

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