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## Ortho-Parahydrogen Mixer, Catalysts, Measurement Devices and their Application

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# Ortho-Parahydrogen Mixer, Catalysts, Measurement Devices and their Application

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**Abstract.** For the majority of low temperature hydrogen applications the ortho- to parahydrogen (o-p-H<sub>2</sub>) spin configuration plays a vital role. Examples are liquid storage (heat of conversion) or neutron moderation (unequal cross section). Decreasing temperatures below ambient imply higher equilibrium p-H<sub>2</sub> ratios. Often, rapid conversion close to the equilibrium is beneficial. The rather slow natural conversion can be sped up for example by catalytic contact to paramagnetic substances. For this, the paper gives an overview on published isothermal conversion catalyst data at LN<sub>2</sub> temperature. Furthermore, an enhanced Catalyst Test Cryostat (CTC) facilitating new adiabatic and isothermal o-p-H<sub>2</sub> catalyst conversion measurements is presented. Precise concentration determination is decisive. Hence, two commercial analyzers, essential for isothermal conversion measurements, using speed of sound or thermal conductivity will be compared to the performance of the independent adiabatic CTC results. Obtained activity data on an industrial catalyst at ≈77.3 K will be provided. Finally, a novel process, batch and closed cycle, providing mixtures with p-H<sub>2</sub> contents ranging from 0.25 to ≈1.00 is introduced. The latter enables e.g. neutron moderation at stable, non-equilibrium o-p-H<sub>2</sub> ratios.

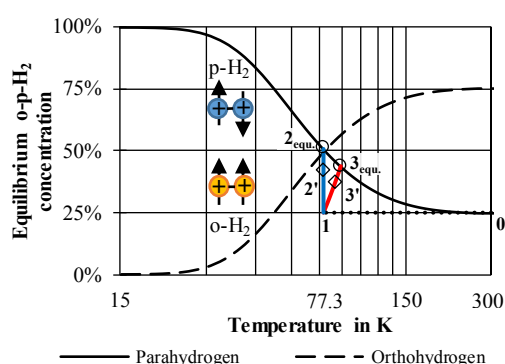
## 1. Introduction

The Hydrogen molecule consists of two atoms with a proton electron pair each. Two nuclear spin isomers can be distinguished: orthohydrogen o-H<sub>2</sub> with its parallel proton spin or triplet state as well as parahydrogen p-H<sub>2</sub> with anti-parallel proton spin or singlet state. At ambient temperature, the two forms appear in a 3:1 composition, the so-called n-H<sub>2</sub>. At lower temperatures a Boltzmann distribution dependent on absolute temperature leads to changed equilibrium e-H<sub>2</sub> compositions for example 0.49/0.51 o-p-H<sub>2</sub> at 77.3 K (LN<sub>2</sub> at 1 bar(a)) or 0.002/0.998 o-p-H<sub>2</sub> at 20.4 K (LH<sub>2</sub> at 1 bar(a)) as presented in Figure 1. A temperature change implies a conversion potential to the original o-p-H<sub>2</sub> mix. This may take place due to the slow natural conversion or among other mechanisms via catalytic reactions on paramagnetic substances. Latter are often investigated by feeding n-H<sub>2</sub> or e-H<sub>2,77.3 K</sub> at a certain temperature, pressure and space velocity (inverse residence time) measuring the changed

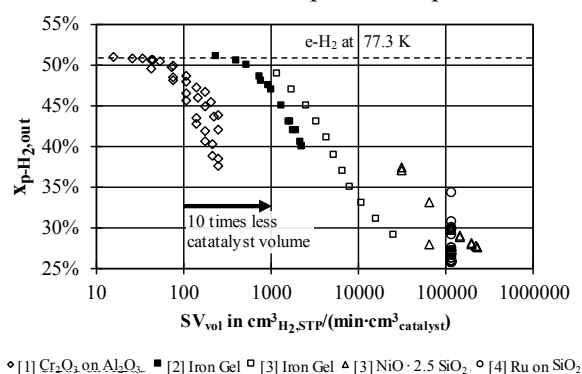


o-p-H<sub>2</sub> ratio after isothermal or adiabatic reaction. In any case, an accurate o-p-H<sub>2</sub> composition determination is required. Methods like spectroscopy or the measurement of vapor pressure, thermal conductivity or speed of sound have been used in the past.

Many paramagnetic substances have been tested and published for their conversion activity at a broad range of reaction conditions. Extensive results investigated under similar conditions on the other hand are rare to find. Figure 2 shows processed historical data [1 to 4] of different catalyst specimens. Chromium oxide shows the poorest performance and is outperformed by iron gel, nickel oxide and ruthenium-based catalysts. Up to two orders of magnitude less catalyst volume for the same conversion separate the specimens. The original catalysts are not available anymore. However, *Oxisorb*® (new brand is *ALPHAGAZ*™) *Purifier O<sub>2</sub>-free* (banned in EU since Q3/2017) may be seen as substitutes for Cr<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> that was used in [1]. Iron gels such as used in [2, 3] are commercially available as *IONEX Type OP*. NiO·2.5 SiO<sub>2</sub> [3], better known as *APACHI-1*, is no longer available at all. Metallic ruthenium on SiO<sub>2</sub> as used in [4] can be fabricated based on the published procedures.



**Figure 1.** e-H<sub>2</sub> composition and isothermal (1→2') or adiabatic (1→3') conversion at or starting from ≈77.3 K.



**Figure 2.** Historical o-p-H<sub>2</sub> isothermal conversion test data of n-H<sub>2</sub> feed at ≈77.3 K of different catalyst specimens.

In this work catalysts are tested through cool down of n-H<sub>2</sub> to ≈77.3 K (0→1) followed by isothermal conversion (T=const.) in LN<sub>2</sub> (1→2') or adiabatic conversion (h=const.) in vacuum (1→3') as shown in Figure 1. If the catalyst is large and active, fed with a small H<sub>2</sub> flow, the equilibrium e-H<sub>2</sub>, 2<sub>equ.</sub> or 3<sub>equ.</sub>, could be almost reached. Novel results (Figure 7) are now comparable to historical data.

## 2. O-p-H<sub>2</sub> Catalyst Test Cryostat for 77.3 K

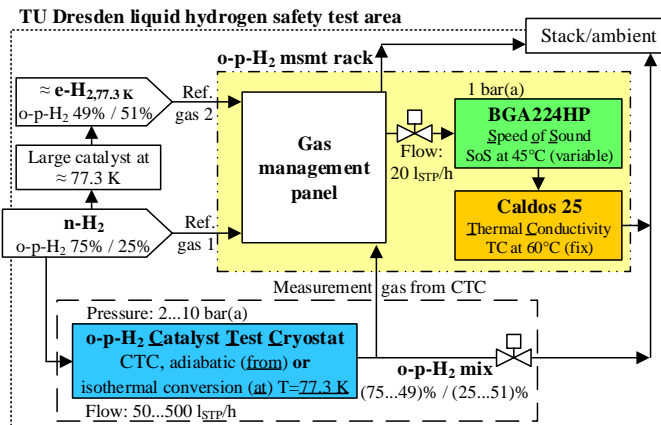
An enhanced adiabatic [5, 6, 7] and isothermal o-p-H<sub>2</sub> Catalyst Test Cryostat (CTC) including o-p-H<sub>2</sub> measurement suite has been engineered, commissioned as well as examined for its accuracy. With the new cryostat, up to 20-times larger space velocities can be realized, the reaction pressure is adjustable, the handling has been simplified and the reliability could be increased. The expected accuracy of the measurement is in the same range as the previous adiabatic cryostat of absolute ±0.5 % p-H<sub>2</sub> [6].

Figure 3 shows the block diagram of the equipment for adiabatic and isothermal o-p-H<sub>2</sub> catalyst tests. The main parts are the CTC and a measurement rack, where a speed of sound (SoS) as well as a thermal conductivity (TC) measurement device are set up. A gas management panel allows the feed of reference gases n-H<sub>2</sub>, e-H<sub>2,77.3 K</sub> or gas from the CTC outlet to the measurement suite. Everything is embedded in the liquid hydrogen safety test area at TU Dresden. Figure 4 presents a process flow diagram of the CTC. N-H<sub>2</sub> gets fed (≤0.0126 g/s) to two heat exchangers in a LN<sub>2</sub> dewar and cooled close to 77.3 K. Adiabatic measurements are performed in a vacuum enclosure. The heat of conversion results in a temperature increase (because of the conversion to more p-H<sub>2</sub>) as shown in Figure 1.

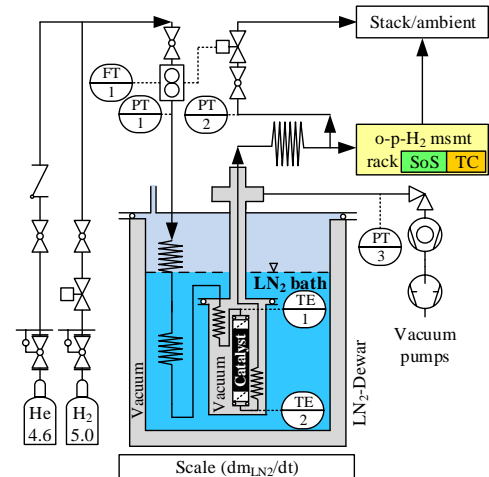
With equation (1), the outlet p-H<sub>2</sub> concentration  $x_{p-H_2,out}$  can be evaluated [6, 8, 9] using  $T_{in}$ ,  $T_{out}$  (2x Pt100 in H<sub>2</sub> flow and calibrated in LN<sub>2</sub>),  $p_{in}$ ,  $p_{out}$  and the corresponding specific enthalpies  $h$  as accurate as now absolute ±0.4 % p-H<sub>2</sub>. But, too small H<sub>2</sub> flows result in a systematic error due to thermal conduction of the catalyst (tube) to the 77.3 K inlet and not in adiabatic ( $h=const.$ ) conditions.

$$x_{p-H_2,out} = \frac{(x_{o-H_2,in} \cdot h_{o-H_2,in} + x_{p-H_2,in} \cdot h_{p-H_2,in}) - h_{o-H_2,out}}{h_{p-H_2,out} - h_{o-H_2,out}} \quad (1)$$

For isothermal measurements, the vacuum housing is omitted so that the reactor is LN<sub>2</sub>-bath cooled. Afterwards, the outlet o-p-H<sub>2</sub> composition must be analyzed by for example SoS or TC.



**Figure 3.** Block diagram of the equipment for adiabatic and isothermal o-p-H<sub>2</sub> catalyst tests.



**Figure 4.** Process flow diagram of the Catalyst Test Cryostat (CTC).

### 3. O-p-H<sub>2</sub> composition determination

For analyzing the p-H<sub>2,out</sub> concentration two measurement devices for a continuous flow as described in Table 1 have been commissioned and compared to the well-characterized adiabatic conversion.

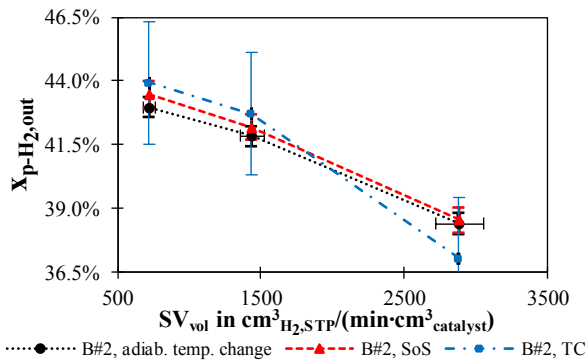
**Table 1.** Information on used o-p-H<sub>2</sub> measurement equipment.

Measured fluid property	Company	Model	Absolute accuracy in % p-H <sub>2</sub>
Speed of Sound, SoS, in absolute m/s	SRS	BGA244HP	±0.2...1.1 % (1-pt. cal., 45°C)
Thermal Conductivity, TC, factory cal., in % p-H <sub>2</sub>	ABB	Caldos 25	±2.4 % (data sheet)

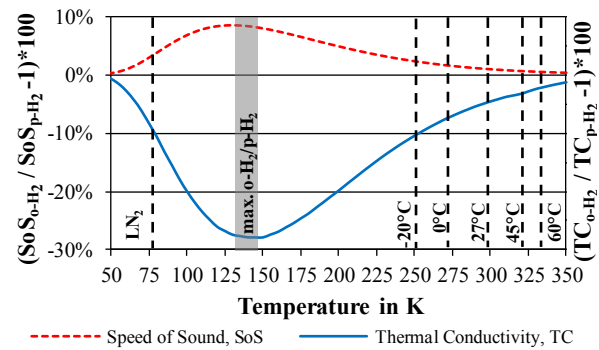
The speed of sound measurement results in absolute m/s along with gas temperature and pressure inside the devices cavity. An internal heater allows the stabilization of the temperature but its use is not required. First measurements have been performed at increased temperatures around 45°C. After a single gas calibration (n-H<sub>2</sub>) has been performed, the absolute accuracy at 45°C is ±0.2 % p-H<sub>2</sub> for a n-H<sub>2</sub> feed to 1.1 % for a pure p-H<sub>2</sub> feed. Switching between n-H<sub>2</sub> and e-H<sub>2,77.3 K</sub> in first tests show fluctuation range of absolute ±0.3 % p-H<sub>2</sub> for both. Definite values require a more thorough analysis.

The thermal conductivity device (is factory two-point calibrated) using a n-H<sub>2</sub>/N<sub>2</sub> mixture and n-H<sub>2</sub> to simulate the difference between n-H<sub>2</sub> and pure p-H<sub>2</sub>. It is more slow than the SoS device because it requires to heat up 1.5 h and unfortunately it operates at fixed 60°C. A frequent recalibration with n-H<sub>2</sub> seems necessary. Its accuracy is ±2.4 % p-H<sub>2</sub> according to the data sheet.

Figure 5 shows a simultaneous measurement of B#2 (Table 2) with first an adiabatic change in temperature in the CTC, followed by speed of sound and thermal conductivity. The feed of 20 l<sub>STP</sub>/h (flow referenced to 273.15 K and 101325 Pa) from the CTC outlet was guided first to the SoS and then to the TC. All three procedures show similar results. The TC fluctuates more around the measured p-H<sub>2</sub> value than the SoS and adiabatic temperature change for unknown reasons. Figure 6 shows the prospective improvements by lowering the temperature of the measured o-p-H<sub>2</sub> mixture using SoS or TC. The reference temperature is set to 300 K (ambient). At 0°C the o-H<sub>2</sub> to p-H<sub>2</sub> difference or ratio increases for SoS and TC by a factor of 1.6 compared to 300 K and for -20°C by a factor of ≈2.2 for both. Optimal temperatures of 130...145 K result in a factor of 8.8 (SoS) or 6.2 (TC) of increased ratio between o-H<sub>2</sub> and p-H<sub>2</sub>. The TC is fixed to 60°C, but the SoS allows temperatures down to -20°C.



**Figure 5.** Comparison of simultaneous adiabatic conversion in CTC vs. SoS and TC measurement.



**Figure 6.** Temperature-dependent ratio between o-H<sub>2</sub> and p-H<sub>2</sub> of SoS and TC [8, 9].

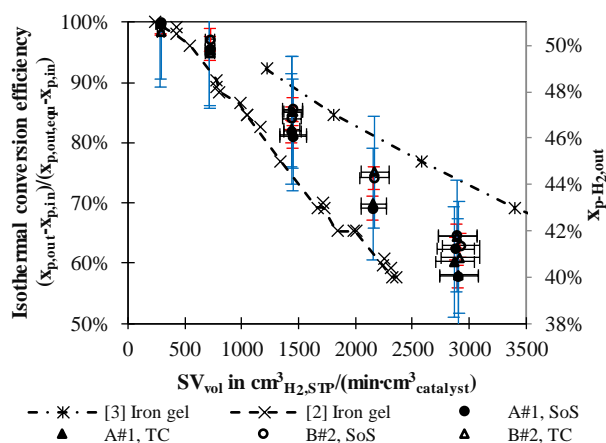
#### 4. Adiabatic and isothermal conversion results of IONEX Type OP at 77.3 K

As reference catalyst, measurement results of IONEX Type OP are presented in this paper. Two different charges A# and B# as detailed in Table 2 of diverse resellers and age have been investigated.

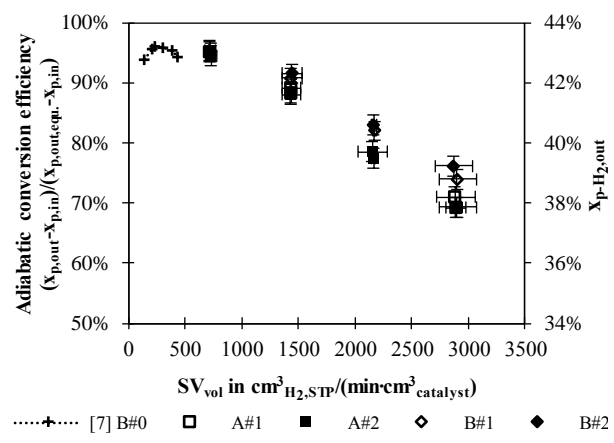
**Table 2.** Tested catalyst specimen: IONEX Type OP (Iron gel).

Supplier	Name	Charge nr.	Year	Samples	Code
Sigma-Aldrich	371254 Ferric hydroxide oxide HFeO <sub>2</sub>	MKBV5321V	2017	2	A#1, A#2
C*Chem	OP Catalyst, Hydrous Ferric Oxide	0111233-11	2001	2	B#1, B#2, (B#0 [7])

The activation procedure pursuing the maximum removal of adsorbed water was the following: Flow of 0.1 l<sub>STP</sub>/min dry N<sub>2</sub> at 120°C and 1 bar(a) for 16 h.



**Figure 7.** Isothermal conversion data for IONEX Type OP (vertical error bar for  $X_{p-H_2,out}$ ,  $\pm 0.5\%$  (SoS) or  $\pm 2.4\%$  (TC) absol. p-H<sub>2</sub>).

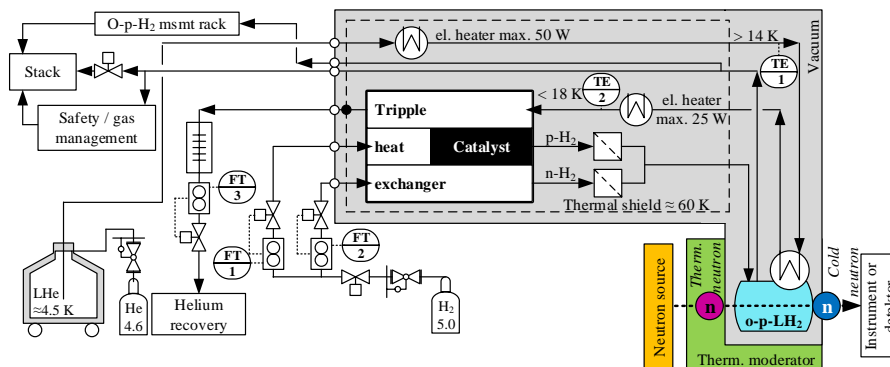


**Figure 8.** Adiabatic conversion data for IONEX Type OP (vertical error bar for  $X_{p-H_2,out}$ ,  $\pm 0.4\%$  absol. p-H<sub>2</sub> for  $SV_{vol} > 1500 \text{ min}^{-1}$ ).

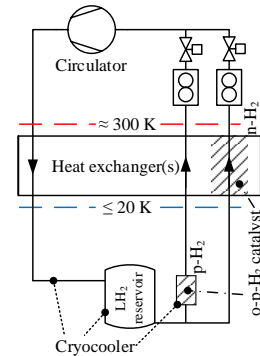
A stainless steel tube of 6 mm outer and 5 mm inner diameter with a length of 150 mm was used resulting in  $\approx 2.9 \text{ ml}$  of catalyst. This leads to volumetric space velocities of  $SV_{vol} = 403 \dots 2889 \text{ min}^{-1}$  for isothermal (see Figure 7) and  $SV_{vol} = 720 \dots 2898 \text{ min}^{-1}$  for adiabatic (see Figure 8) conversion measurements. Isothermal results are in agreement with historic measurements on iron gel [2, 3]. The adiabatic performance is in agreement with previously published data [7] on the same IONEX type OP lot B#0. No sign of aging between A# and B# can be observed.

### 5. O-p-H<sub>2</sub> mixing cryostat

A novel concept for a highly optimized medium flux neutron source [10] proposes variable liquid o-p-H<sub>2</sub> mixtures as moderator fluid. Figure 9 shows a cold helium gas cooled o-p-H<sub>2</sub> mix batch cycle, enabling those stable mixtures for the first time. Results from section 1 to 5 of this paper contributed to the design, commissioning and operation of this test setup in Q3/2017 at TU Dresden's Training Reactor AKR-2 with first o-p-LH<sub>2</sub> neutron moderation tests. Helium cold gas externally cools the LH<sub>2</sub> moderator vessel before it cools down two individual streams of H<sub>2</sub>: a) n-H<sub>2</sub> (without catalyst) and b)  $\approx$  pure p-H<sub>2</sub> (with a large catalyst). The two streams are mixed to the desired liquid o-p-H<sub>2</sub> ratio [11].



**Figure 9.** Schematic batch o-p-H<sub>2</sub> mix cycle with Helium cold gas cooling realized for and operated at Training Reactor AKR-2 (2 W, TU Dresden).



**Figure 10.** Closed o-p-H<sub>2</sub> mixing process [12].

Figure 10 shows a novel concept of a closed o-p-H<sub>2</sub> mixing and stabilizing process based on a cryocooler, instead of usually used pure p-H<sub>2</sub> or uncontrolled o-p-H<sub>2</sub> ratios for cold neutron moderation.

### 6. Conclusion

An enhanced o-p-H<sub>2</sub> catalyst test cryostat for adiabatic and isothermal conversion at  $\approx 77.3$  K including its measurement suite of speed of sound and thermal conductivity has been presented. Historic catalyst data was transformed for comparison and novel measurements of two different charges (source and age) of IONEX Type OP (iron gel) fit well to the published data. A batch and continuous process was introduced, enabling stable p-H<sub>2</sub> contents of 0.25 to  $\approx 1.00$  in LH<sub>2</sub> e.g. as neutron moderating fluid.

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