# SPECIAL PROBLEMS WHEN REALISING THE TRIPLE POINT OF HYDROGEN AS A DEFINING FIXED POINT OF THE ITS-90

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#### ABSTRACT

The two special problems, which appear when realising the triple point of hydrogen as a temperature fixed point due to the influences of the deuterium content and the catalyst, have been investigated by filling a large number of sealed triple-point cells. The cells differ with respect to the deuterium content (29  $\mu$ mol D/mol H to 155  $\mu$ mol D/mol H), type of catalyst (hydrous ferric oxide and gadolinium oxide), catalyst-to-liquid volume ratio (a few per cent to more than 100 per cent) and cell design. At higher catalyst-to-liquid volume ratios, the shape of the melting curve depends on the type of the catalyst, but only the melting temperature of that sample part being in direct contact with the catalyst and thus distorted is changed. For the slope of the dependence of the triple-point temperature on the deuterium content, a preliminary value of (5.2 ± 0.4)  $\mu$ K per  $\mu$ mol D/mol H has been found.

#### **1. INTRODUCTION**

Two special problems appear when realising the triple point of hydrogen as a defining fixed point of the International Temperature Scale of 1990 (ITS-90) [1] at the highest level of accuracy, which differentiate it from the other low-temperature fixed points. First, to ensure that the hydrogen has the prescribed equilibrium composition of the two nuclear-spin isomers (often designated by the prefixes ortho and para), it is necessary to place a suitable spin-conversion catalyst in the fixed-point sample chamber. Second, the concentration of deuterium present in high-purity hydrogen, and thus the triple-point temperature of the sample, depends on the method used for the gas production.

The problem associated with the catalyst has been found to manifest itself as a depression of the melting temperature of that part of the sample in direct contact with the catalyst [2-4]. This depression is suspected to be caused by a weakening of the crystal lattice. The dependence of this depression on the Catalyst-to-Liquid Volume Ratio (CLVR) is observed either only at the beginning of the melting curve, or even throughout the whole curve. The melting curve is measured to realise the triple point, and it may be significantly changed to the extent that there is a shift in the melting temperature with respect to that of non-distorted solid hydrogen. In contrast, the differences in the deuterium concentration for hydrogen samples produced by different methods are so large that differences of the triple-point temperatures of up to several tenths of a millikelvin may occur. This problem has been pointed out already by Pavese and Tew [5] and is analysed in detail by Pavese, *et al.* [6]. It is one of the reasons for the fact that the investigation of hydrogen melting curves is an especially important part of the currently running intercomparison of sealed triple-point cells [2].

These two hydrogen problems have been investigated by filling and measuring a large number of sealed triple-point cells. The cells differ with respect to the deuterium content, type of catalyst, CLVR and cell design. These parameters have been varied from cell to cell in such a way that the various effects can be separated. In this paper, an overview of the investigated cells and the method applied for measuring the melting curves is given. Then, the obtained results are summarised. The detailed

analysis of the shapes of quite different melting curves enables one to reliably deduce the melting temperatures of those parts of the hydrogen samples which are not distorted by the catalyst. Using these temperature values, the dependence of the triple-point temperature on the deuterium content can be determined. For this dependence, the available literature data are not sufficiently accurate [6]. Besides the joint activities treated in this paper, which are part of the European project MULTICELLS [7], Sakurai [8] and Steele [9] investigate the two hydrogen problems at the moment independently also.

# 2. SEALED CELLS AND MEASUREMENT METHOD

Table 1 contains an overview of the investigated hydrogen sealed cells. These are divided into two principle types: 1) the traditional single-compartment "cells" and 2) the "elements" for multicompartment cells of the IMGC design [10]. The commercial gas sources are given in the footnotes. In many cases these gas sources are just gas distributors and purifiers, and are not the true origin of the gas, which may vary with location and time. As far as isotopic composition is concerned, the method of gas synthesis is of primary interest. The two gases used at NIST originated almost certainly as oil refinery by-product gas and are, therefore, very depleted in deuterium (see [6]). Furthermore, it is most probable that the older gas samples were produced by the electrolysis of water, i.e. they may be also very depleted. The suppliers have specified the gas purity (nominal purity). It is supported by individual analysis results in some cases.

The isotope (D/H) ratio  $R_D \equiv [^2H]/[^1H]$  (<sup>1</sup>H protium, or 'H', <sup>2</sup>H deuterium, or 'D') in µmol D/mol H gives the deuterium content. The values in parentheses are the standard uncertainties. The D/H ratio in a given sample is normally determined by comparison of the mass spectrum to that of a reference hydrogen gas, which has been derived from VSMOW (Vienna Standard Mean Ocean Water, see [11]) by preserving the same isotopic ratio  $R_{D,VSMOW} = 155.74 \mu mol D/mol H$  [12]. It is reported as a dimensionless relative variation  $\delta D_{VSMOW}$  (for details see [6]). The relation between these quantities is  $R_D = R_{D,VSMOW} (\delta D_{VSMOW}+1)$ .

Two different catalysts have been applied: Hydrous Ferric Oxide (HFO) and Gadolinium Oxide (GO). The CLVRs have been estimated using a value of 0.077 g/cm<sup>3</sup> [13] for the density of liquid hydrogen. The bulk densities of HFO and GO amount to about (3 to 4) g/cm<sup>3</sup> [14] and 7 g/cm<sup>3</sup> [14], respectively. But the densities of the uncompressed catalyst powders contained in the NIST and IMGC cells have been measured to be only 0.5 g/cm<sup>3</sup> (NIST, HFO) and 1 g/cm<sup>3</sup> (IMGC, GO). Table 1 contains CLVR estimates, which are based on the powder densities. The usefulness of these estimates is discussed in Section 3.

Since the parameters of the cells and elements differ widely, it is possible to investigate in detail various effects: The comparison of the melting curves of cells H<sub>2</sub>-211, H<sub>2</sub>-212, H<sub>2</sub>-214, H<sub>2</sub>-1, H<sub>2</sub>-3, 2H<sub>2</sub>, 4H<sub>2</sub>, and 5H<sub>2</sub> yields information on the influence of the catalyst HFO. The designs of these cells are quite different, especially concerning the thermal conditions and the location of the catalyst in the sample chamber. Cells  $10H_2$  to  $14H_2$  have been filled using hydrogen samples having practically the same D/H ratio, but the spread of their CLVRs is large. In addition to the influence of the catalyst GO on the melting curves, the repeatability of the melting temperature can be also checked comparing these cells. Cells H<sub>2</sub>-211 and H<sub>2</sub>-214 as well as element Eb1H2 contain the same gas, but not the same catalyst. This enables one to answer the question whether the catalysts change the melting temperatures of those sample parts not in direct contact with them.

The participating institutes have investigated the melting curves and different parameters of the hydrogen cells and elements, respectively, in accordance with a detailed protocol in order to obtain results, which can be compared directly. The protocol is essentially based on the measurement

program for the comparison of sealed triple-point cells described in [2]. For measuring a melting curve, the sample was heated through the solid-to-liquid phase transition under nearly isothermal conditions by the intermittent application of heat. After each heat pulse, the cell was allowed to come to thermal equilibrium. At each equilibrium temperature throughout the transition, the thermometer resistances were accurately measured and the fraction F of sample melted was determined from the heat applied considering the complete melting curve and the heat capacity  $C_{\rm C}$  of the cell. During each investigation of a cell, the following parameters were determined: thermal resistance  $R_{\rm CS}$  between the metal parts of the cell and the solid phase, thermal resistance between the cell and its surroundings, heat capacity  $C_{\rm C}$  of the cell, heat of fusion  $Q_{\rm HF}$ , heat leak to the cell and thermal recovery time constant. The F dependencies of both  $R_{CS}$  and the thermal recovery time were investigated. The possible occurrence of a long creeping after the first part of the recovery, which corresponds usually to an exponential relaxation, was carefully checked. Using these parameters, it was possible to estimate dynamic and static temperature measurement errors. The experiments were performed so that these errors were smaller than 0.03 mK. Before the measurements of the final melting curves were made, it was checked that the ortho-para conversion of the hydrogen sample into its equilibrium composition had occurred. For this purpose, several consecutive preliminary melting curves were measured, allowing various time periods for the conversion to take place (with the sample being maintained in the liquid phase very near to the triple-point temperature during those periods). At PTB, using at least three capsule-type resistance thermometers reduced the influence of possible thermometer instabilities. Comparing the readings of ac and dc bridges yielded an additional check of the measurements of the thermometer resistances.

Due to the depression of the melting temperature of those parts of the sample in direct contact with the catalyst, the total heat of fusion can be only determined if the pre-melting of these sample parts is considered. Otherwise, the wrong impression would arise that the heat of fusion depends strongly on the amount of catalyst [20]. For very large CLVRs and some catalysts, the temperature dependence of the heat capacity  $C_{\rm C}$  may show a maximum or "abnormality" below the melting temperature of the non-distorted solid hydrogen due to the pre-melting [4, 8]. This anomaly could be explained by the fact that a large portion of the distorted sample melts at nearly the same temperature. But in any case, the pre-melting causes an increase of  $C_{\rm C}$ . For some of the cells, this increase has been investigated in detail starting at temperatures of a few 0.1 K below the triple point. To determine the portion  $Q_{\rm PM}$  of the total heat of fusion  $Q_{\rm HF}$  that is necessary for the pre-melting, the measured temperature dependence of  $C_{\rm C}$  has been analysed considering the  $C_{\rm C}$  value determined at the sufficiently low starting temperature. (Without pre-melting,  $C_{\rm C}$  would increase at most proportionally to the temperature cubed, i.e. only about 5% within the temperature range of 0.2 K below the triple point.)

## **3. RESULTS**

In this paper, only a short overview of the comprehensive results can be given. The experiments performed at PTB are described in detail in [21]. A comprehensive description of the final results will be published elsewhere.

Figures 1 and 2 show melting curves, which have been obtained for both cells and elements containing either HFO or GO as the catalyst. The measured equilibrium temperatures  $T_e$  are shown as dependent on F. This representation enables one to best distinguish the different parts of the curves. In the often used representation  $T_e$  versus 1/F, the flat parts of the melting curves are largely compressed, which overemphasizes the importance of the beginning of the melting (see [3]). This initial part of the melting curve may, however, be strongly influenced by the depression of the melting temperature due to the catalyst.

For all cells and elements having sufficiently small CLVRs, the obtained melting curves are very flat at higher fractions of sample melted. We refer to the flat part of a curve as the "plateau" and the equilibrium temperature at the middle of the plateau is  $T_{\rm P}$ . The plateau results from the melting of those sample parts which are not distorted by the catalyst. Its width is usually smaller than 0.1 mK, i.e. the "natural width" of the melting range of high-purity, non-distorted solid hydrogen amounts to at most 0.1 mK. Thus, it seems reasonable to say that pre-melting occurs at least up to a temperature, which is smaller than the plateau temperature by only 0.2 mK. Using this limit, it is possible to estimate  $Q_{\rm PM}$  reliably.



**Figure 1** (on the left): Melting curves of hydrogen cells containing HFO as the catalyst: The parameters of the cells are listed in Table 1. To enable a direct comparison of the curves, in each case the temperature difference  $(T_e-T_P)$  versus the fraction of sample melted *F* is shown.

**Figure 2** (on the right): Melting curves of hydrogen cells and elements containing GO as the catalyst: The parameters of the cells are listed in Table 1. To enable a direct comparison of the curves, in each case the temperature difference  $(T_e-T_P)$  versus the fraction of sample melted *F* is shown.

For cells containing HFO as the catalyst (Figure 1), three different shapes of the melting curves have been obtained. At relatively low CLVRs (H<sub>2</sub>-212, H<sub>2</sub>-3, 5H<sub>2</sub>), the plateau is already reached at about F = 0.1, i.e. the width of the whole melting curve in the F range from 0.1 to 0.9 amounts to at most 0.1 mK. Medium CLVRs (H<sub>2</sub>-1, H<sub>2</sub>-214) cause a pronounced rounding of the beginning of the melting curve, but a plateau exists at higher F values. If the CLVR is large (e.g.  $2H_2$ ,  $4H_2$ ,  $H_2$ -211), the catalyst depresses the melting temperature of the whole sample and no perfectly flat plateau is observed. The excellent agreement between the results obtained at NIST and PTB for cell H<sub>2</sub>-212 shows that the measured equilibrium temperatures are influenced by thermal effects by no more than a few 0.01 mK. It is interesting to note that the pre-melting of the two cells H<sub>2</sub>-212 and H<sub>2</sub>-1 is quite different: The ratio  $Q_{\rm PM}/Q_{\rm HF}$  of cell H<sub>2</sub>-1 is larger than that of cell H<sub>2</sub>-212 by a factor of about two. On the other hand, in cell H<sub>2</sub>-212 about 10 % of the hydrogen sample is strongly distorted by the catalyst (melting temperature depressed by more than 2 mK), but only about 5 % in cell H<sub>2</sub>-1. Furthermore for HFO, the CLVR values based on the powder density sufficiently describe the influence of the catalyst on the melting curves only in some cases. Only for the NIST cells, do the CLVRs correlate nearly with the shape of the measured curves. Since the melting temperatures are depressed for those sample parts in very close contact with the catalyst, the particle size and the activation procedure may influence the effective density of the catalyst. The influence of these different factors has to be investigated in more detail, but the existence of a flat plateau seems to be a sufficient criterion for verifying that the melting temperature of non-distorted hydrogen is reached.

The comparison of Figure 1 with Figure 2 shows that the influence of GO on the shape of the melting curves differs from that of HFO. At medium CLVRs (10H<sub>2</sub>, 12H<sub>2</sub>, 14H<sub>2</sub>), a shoulder is usually

followed by an increase of the melting temperature to the plateau value within a narrow F range, i.e. the shape is stepwise. The F value, at which the step occurs, correlates fairly well with the CLVR based on the density of the powder having a particle size of about 1 µm. The shoulder may be caused by the fact that a large portion of the distorted solid hydrogen has a melting temperature which is smaller than the plateau temperature by about 3 mK. The elements E2H<sub>2</sub> and E3H<sub>2</sub> have been investigated both at INTiBS and at PTB. The results of the two institutes coincide again quite well. For these two elements, the scattering of the measured melting temperature is a little larger than for the other cells due to large thermal resistances  $R_{CS}$  at high fractions of sample melted (up to about 50 K/W). Nevertheless, high-quality melting curves have been measured by checking carefully the thermal conditions according to the agreed protocol and determining the thermometer overheating with respect to the solid phase at each F.

The analysis of the shapes of the melting curves establishes that the plateau temperatures should be used to determine the dependence of the triple-point temperature on the deuterium content. In each case the temperature value at the middle of the plateau was chosen for the following reasons: Some of both the cells and the elements have very large internal thermal resistances  $R_{\rm CS}$  at high fractions of sample melted. In these cases, the often applied extrapolation to the liquidus point (F = 1) is dangerous because the impact of the thermal conditions on the measured melting temperatures increases strongly with increasing F. Furthermore, it is not clear whether this extrapolation is useful in reducing the influence of impurities when realising the hydrogen triple point. Considering the behaviour of the relevant impurities [22] as well as the small first cryoscopic constant of hydrogen [23], the influence of impurities should not broaden the plateau by more than a few 0.01 mK if high-purity hydrogen is used (e.g. for hydrogen 99.999 % chemical purity, the maximum estimate for the shift of the liquidus temperature by impurities amounts to about 0.07 mK [23]). If  $R_{CS}$  is large, thermal effects may easily cause a similar broadening of the plateau. Neon is in principle the most influential impurity because it is known to change the melting temperature, but it is not likely to be present in hydrogen [22]. Also, a simple extrapolation of T versus 1/F to F = 1 does not reduce definitely the influence of impurities because at least neon seems to be soluble in solid hydrogen [13].

Figure 3 shows the results for the dependence of the melting temperature at the middle of the plateau  $T_{\rm P}$  on the D/H ratio  $R_{\rm D}$ . For the PTB data, the plateau temperatures are directly related to that of cell H<sub>2</sub>-1. Only this cell has been measured very often during the whole investigation period, i.e. all other cells have been directly compared with it. Such a direct comparison with a reference cell decreases significantly the possible influence of thermometer instabilities on the results and enables one to check regularly the whole measurement equipment. (Cell  $H_2$ -1 seems to contain hydrogen, which is very depleted in deuterium. This is valid also for other relatively old cells, e.g. H<sub>2</sub>-3.) The results of other institutes are considered by adding their differences between plateau temperatures of the investigated cells or elements to the temperature values measured at PTB. For instance, the differences between the plateau temperatures of elements E2H<sub>2</sub> and E3H<sub>2</sub> determined at INTiBS and PTB coincide quite well within the combined uncertainties. Especially the good agreement of the results obtained for the NIST cells and element  $Eb1H_2$  supports the conclusion that the melting temperature of the sample parts not in direct contact with the catalyst is not significantly influenced by the catalyst. The straight line in Figure 3 results from a linear fit to the data. Its slope amounts to  $5.2 \,\mu\text{K}$  per  $\mu\text{mol D/mol H}$ . Considering both the uncertainties of the plateau temperatures and the D/H ratios, a standard uncertainty of this slope of 0.4 µK per µmol D/mol H has been deduced. These are preliminary values since the inclusion of further results for the cells and elements listed in Table 1 will hopefully decrease the uncertainty. This slope is close to that obtained in [24] for larger concentration mixtures (5.6  $\mu$ K per umol D/mol H). The uncertainty budget in this work for the plateau temperatures contains the following components (typical temperature equivalents of the standard uncertainties are given in parentheses): plateau width and influence of impurities (0.03 mK), static and dynamic temperature measurement errors (0.02 mK), non-repeatability of the plateau values (0.02 mK), resistance measurement (0.02 mK), thermometer instability (0.03 mK). The uncertainty has been estimated individually for each plateau temperature. In the uncertainty budget for the results obtained by INTiBS and NIST, furthermore, the uncertainty of the reported differences between plateau temperatures is considered. As specified in Table 1, the maximum uncertainty of the D/H ratio is 6  $\mu$ mol D/mol H, the temperature equivalent of which amounts to about 0.03 mK. Thus, in view of typical standard uncertainties of the plateau temperatures of 0.05 mK, the uncertainty of the slope of  $T_P(R_D)$  is dominated by the effects influencing the realisation and measurement of the plateau temperatures.



**Figure 3**: Dependence of the equilibrium plateau temperature  $T_P$  on the D/H ratio  $R_D$ . The temperature values for different cells and elements (see Table 1), respectively, are drawn relative to the plateau temperature  $T_{Ref}$  of the reference cell H<sub>2</sub>-1. In the legend, the testing institute is given after the slash.

## 4. CONCLUSIONS

For a large number of different sealed triple-point cells, the melting temperatures of those parts of the hydrogen samples not in direct contact with the catalyst have been determined on the basis of a careful analysis of the shapes of the melting curves. Using these melting-temperature data, the slope of the dependence of the triple-point temperature on the deuterium content has been found to be  $(5.2 \pm 0.4) \mu K$  per  $\mu mol D/mol H$ . This preliminary value should be checked as soon as further data are available, from both additional data for the cells and elements listed in Table 1 and independent data of other groups. The final value is urgently needed for re-defining the triple point of equilibrium hydrogen as a defining fixed point of the ITS-90 in order to remove the ambiguity due to the influence of the isotopic composition. Possible ways in which the hydrogen fixed points could be re-defined are discussed in [6].

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#### REFERENCES

- 1. Preston-Thomas H., *Metrologia*, 1990, **27**, 3-10, 107
- Fellmuth B., Berger D., Wolber L., In: *Proceedings of TEMPMEKO '99*, 7th International Symposium on Temperature and Thermal Measurements in Industry and Science, J.F. Dubbeldam, M.J. de Groot (ed.), Delft, IMEKO / NMi Van Swinden Laboratorium, 1999, pp. 233-238
- 3. Fellmuth B., Berger D., Wolber L., BIPM Com. Cons. Thermométrie 20, 2000, Document CCT/99-07
- 4. Sakurai H., In: *Proceedings of TEMPMEKO '99*, 7th International Symposium on Temperature and Thermal Measurements in Industry and Science, J.F. Dubbeldam, M.J. de Groot (ed.), Delft, IMEKO / NMi Van Swinden Laboratorium, 1999, pp. 124-128
- 5. Pavese F., Tew W., BIPM Com. Cons. Thermométrie 20, 2000, Document CCT/2000-19
- 6. Pavese F., Tew W.L., Steele A.G., These Proceedings, 2001, to be published
- 7. Pavese F., de Groot M., Fellmuth B., Head D., Hermier Y., Szmyrka-Grzebyk A., Zanin L., These Proceedings, 2001, to be published
- 8. Sakurai H., These Proceedings, 2001, to be published
- 9. Steele A.G., These Proceedings, 2001, to be published
- 10. Pavese F., Ferri D., Peroni I., Steur P.P.M., These Proceedings, 2001, to be published
- 11. Gonfiantini R., *Nature*, 1978, **271**, 534-536
- 12. IUPAC Comm. on Atomic Weights and Abundances, Pure Appl. Chem., 1998, 70, 217-235
- 13. Pavese F., Molinar G., *Modern Gas-Based Temperature and Pressure Measurements*, New York, Plenum Press, 1992, 514 pp.
- 14. Chemical Rubber Company, *Handbook of Chemistry and Physics*, Boca Raton, FL, CRC Press, R.C. Weast (ed.), 61<sup>st</sup> Edition, 1980, p. B-109; D.R. Lide (ed.), 81<sup>st</sup> Edition, 2000, p. 4-66
- 15. Tew W.L., In: *Proceedings of TEMPMEKO '96*, 6th International Symposium on Temperature and Thermal Measurements in Industry and Science, P. Marcarino (ed.), Torino, Levrotto & Bella, 1997, pp. 81-86
- 16. Head D.I., Rusby R.L., Martin J.E., *Cryogenic Triple Point Cells at NPL*, NPL Report QM116, Teddington, National Physical Laboratory, 1995, ISSN 1361-4045, 21 pp.
- Fellmuth B., Seifert P., Rudloff H., In: *Proceedings of TEMPMEKO '96*, 6th International Symposium on Temperature and Thermal Measurements in Industry and Science, P. Marcarino (ed.), Torino, Levrotto & Bella, 1997, pp. 93-98
- 18. Pavese et al., Metrologia, 1984, 20, 127-144
- 19. Pavese F., Ferri D., Giraudi D., Steur P.P.M., In: *Temperature, Its Measurement and Control in Science and Industry*, Vol. 6, J. F. Schooley (ed.), New York, Am. Inst. of Phys., 1992, pp. 251-256
- 20. Ancsin J., BIPM Com. Cons. Thermométrie 14, 1982, Document CCT/82-7
- 21. Fellmuth B., Berger D., Wolber L., Report, EU Project MULTICELLS, Contract N° G6RD-CT-1999-00114, July 2001, to be published
- 22. Ancsin J., Metrologia, 1977, 13, 79-86
- 23. Mangum B.W., Bloembergen P., Fellmuth B., Marcarino P., Pokhodun A.I., BIPM Com. Cons. Thermométrie **20**, 1999, Document CCT/99-11
- 24. Bereznyak N., Bogoyavlenskii I., Karnatsevich L., Logan V., Sov. Phys. JETP, 1970, 30,1048-1049

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S/N	Manu-	Model	Date of	<b>Gas Source</b>	Gas	D/H Ratio	H <sub>2</sub> Content	Catalyst	Catalyst	CLVR	Testing
	Facturer		Sealing		Purity	µmol D/mol H			Content		Institutes
H <sub>2</sub> -211	NIST	Type II [15]	May 2000	Matheson <sup>1</sup> )	$6N^{4}$ )	45.8 (0.6)	56 mmol	HFO	0.70 g	0.9	NIST
		(316 SS / Cu)									
H <sub>2</sub> -212	NIST	Same as H <sub>2</sub> -211	July 2000	MG Industries <sup>2</sup> )	6N	29.1(0.6)	68 mmol	HFO	0.20 g	0.2	NIST, PTB
H <sub>2</sub> -214	NIST	Same as H <sub>2</sub> -211	July 2000	Same as H <sub>2</sub> -211	6N	45.8 (0.6)	83 mmol	HFO	0.18 g	0.2	NIST
H <sub>2</sub> -1	NPL	Wide SS/Cu [16]	June 1987	Air Liquide	6N		55 mmol	HFO	1 g	1.4	NPL, PTB
H <sub>2</sub> -3	PTB	C (Cu) [17]	Sept. 1993	Linde AG	6N		205 mmol	HFO	1.6 g	0.6	PTB
$2H_2$	IMGC	C [18, 19]	Jan. 1983	Precision Gas	6N	Available in	55 mmol	HFO	1.5 g	2.1	PTB, IMGC
				Products		June					
$4H_2$	IMGC	Bter [18, 19]	Dec. 1986	Same as 2H <sub>2</sub>	6N	Same as 2H <sub>2</sub>	$\leq 60 \text{ mmol}$	HFO	1.2 g	≥1.5	PTB
5H <sub>2</sub>	IMGC	Large type	March 1987	Italian Company	6N	Same as 2H <sub>2</sub>	337 mmol	HFO	1.5 g	0.3	PTB
		[18, 19]		SIAD					-		
10H <sub>2</sub>	IMGC	Same as 4H <sub>2</sub>	Aug. 1999	$MG^{3}$ )	$5N^{4}$ )	123 (6)	69 mmol	GO	1.1 g	0.5	PTB
11H <sub>2</sub>	IMGC	Same as 4H <sub>2</sub>	Oct. 1999	$MG^{3}$ )	6N	124 (6)	50.1 mmol	GO	1.1 g	0.9	INTiBS
12H <sub>2</sub>	IMGC	Same as 4H <sub>2</sub>	Oct. 1999	Same as 11H <sub>2</sub>	6N	124 (6)	90.8 mmol	GO	1.1 g	0.5	IMGC
13H <sub>2</sub>	IMGC	Same as 4H <sub>2</sub>	Oct. 1999	Same as 11H <sub>2</sub>	6N	124 (6)	134 mmol	GO	1.1 g	0.3	PTB
$14H_2$	INTiBS /	Bbis [18, 19]	Nov. 1999	Same as 11H <sub>2</sub>	6N	124 (6)	82,3 mmol	GO	1.1 g	0.55	INTiBS, PTB
	IMGC								-		
$E2H_2$	IMGC	M-cell [10]	March 2000	MG <sup>3</sup> ) ISO-TOP	5N	154.9 (1.6)	63.5 mmol	GO	0.35 g	0.2	PTB, INTiBS
E3H <sub>2</sub>	IMGC	Same as E2H <sub>2</sub>	March 2000	MG <sup>3</sup> ) ISO-TOP	5N	46.2 (3.2)	65.5 mmol	GO	0.35 g	0.25	PTB, INTiBS
E4H <sub>2</sub>	IMGC	Same as E2H <sub>2</sub>	May 2001	MG <sup>3</sup> ) ISO-TOP	5N	91.6 (0.8)	64.0 mmol	GO	0.35 g	0.25	IMGC
Eb1H <sub>2</sub>	IMGC	New M-cell [10]	March 2001	Same as H <sub>2</sub> -211	6N	45.8 (0.6)	65.5 mmol	GO	0.35 g	0.2	PTB

Table 1: Overview of the investigated hydrogen single cells and elements for multi-compartment cells of IMGC design

<sup>1</sup>) Matheson Gas Products, Gloucester, MA, USA
<sup>2</sup>) MG Industries, Malvern PA
<sup>3</sup>) Messer Griesheim
<sup>4</sup>) 5N: 99.999 % etc.