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Sieverts apparatus and methodology for accurate determination of hydrogen uptake by light-atom hosts

T.P. Blach, E.MacA. Gray *

Nanoscale Science and Technology Centre, Griffith University, Brisbane 4111, Australia

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Abstract

Accurate determination of the quantity of hydrogen absorbed by a potential hydrogen storage material is crucial to progress in the field. The most common techniques for measuring hydrogen uptake from the gas phase by a solid host, the Sieverts technique and gravimetry, both become susceptible to systematic errors as the density of the host material decreases. We focus here on the Sieverts technique, which in a poorly designed apparatus may produce errors ∼100% in the quantity of absorbed hydrogen owing to a realistic 25% error in the density of a light-atom sample. Using hydrogen absorption isotherms measured for low-density materials, including carbon nanotubes, potassium-intercalated graphite and lithium nitride, we show that designing the Sieverts apparatus with carefully chosen volumes greatly lessens the impact of uncertainty in the sample density. Rules-of-thumb for the volumes in the apparatus and the volume occupied by the sample itself, and a figure of merit for the sensitivity of the system to changes in the hydrogen content of the sample, are introduced.

Keywords: Hydrogen absorbing materials; Nitride materials

1. Introduction

Reliable measurement of hydrogen uptake in the laboratory is a vital prerequisite to the real-world application of new hydrogen storage materials, especially to verify claims in the literature and to facilitate meaningful comparisons between sample preparation routes. Interest in high-capacity solid-state hydrogen storage hosts with non-metallic character, based on light elements, especially Li, B, C, N, Mg and Al, is rising rapidly in the pursuit of the US Department of Energy mass density criteria (6 wt.% by 2010; 9 wt.% by 2015) [1]. These materials have much lower densities than classic metal-H systems such as $LaNi_5$-H_2. We show here that this fact has ramifications for the accurate determination of the mass density of absorbed or adsorbed hydrogen.

The most common techniques for measuring hydrogen uptake by a solid host are the Sieverts (manometric) technique and gravimetry, with the focus of this work being on the former technique owing to its practicability and very widespread use. The Sieverts technique is cheap, robust, portable, simple and, when practised with reasonable care, universally accepted as accurate. In the Sieverts technique, a calibrated reference volume is filled with gas to a measured pressure and then opened to the sample chamber, the gas uptake by the sample being calculated from the change in the gas pressure in the system. Hydrogen uptake is represented here by the hydrogen-to-host atomic ratio, *H*/*X*, by analogy with the hydrogen-to-metal ratio for a metal, *H*/*M*.

The authors became aware [2] of problems with the credibility of measurements of hydrogen uptake by low-density hosts using the Sieverts technique, in which a modest uncertainty in the density of the sample was observed to lead to an amplified uncertainty in the hydrogen concentration in the host. Whereas the need to measure temperature and pressure accurately is obvious and widely accepted, the problem of accounting for the sample volume turns out to be more subtle and potentially much more detrimental to the measurement of *H*/*X*.

The Sieverts technique is sensitive to the density of the sample because the volume occupied by the sample must be subtracted from the volume of the empty sample cell in order to calculate *H*/*X*. The difficulty then arises of defining and accurately measuring the volume occupied by a low-density sample with

* Corresponding author. Tel.: +61 7 3735 7240; fax: +61 7 3735 7656.
E-mail address: E.Gray@griffith.edu.au (E.MacA. Gray).

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an effective dimensionality between 2 and 3 owing to its pore structure or a high surface-to-volume ratio. In an extreme case, such as carbon nanofoam [3], it may be practically impossible to define the material density. Furthermore, the X-ray density of a new starting material may not be known until a structure determination has been done, a problem compounded by any change in the sample density owing to hydrogen uptake. The sample volume problem has been pointed out before [4] in the context of high-pressure measurements, but we show here that the problem also occurs at pressures of a few bar.

We note that the alternative gravimetric technique, in which the change in the weight of the sample owing to gas uptake is measured, is likewise sensitive to the sample volume through buoyancy forces on the components of the system immersed in the gas. As the buoyancy force on a system component is the weight of the gas displaced by it, the volume of the sample and hence its density enter the calculation, with the density of the sample becoming more important as it decreases.

This paper reports our findings from experiments and simulations in which real experimental data taken with the Sieverts technique were re-analysed assuming that the density of the sample varied in a range of ±25% about its nominal value. The aim was to construct some design rules which would minimise the sensitivity of the calculated value of H/X to uncertainty in the sample density, while maintaining acceptable sensitivity to changes in the hydrogen content of the sample.

2. Sieverts technique for measuring hydrogen uptake

Fig. 1 shows a generic Sieverts hydrogenator on which the following analysis is based. The analysis applies in principle to any gas. The measurement of hydrogen uptake is made stepwise. Suppose that, at the end of the $k-1$th step, a pressure p_{sys} of hydrogen is present throughout the hydrogenator, which we refer to as the system pressure. The gas in the reference volume is at temperature T_{ref} and the gas in the sample cell is at T_{cell}. The connecting valve, S, is closed to isolate the sample cell, which has an empty volume V_{cell}. A new pressure p_{ref} at temperature T_{ref} is established in the reference volume, V_{ref}. S is then opened and a new value p_{sys} is measured, along with new values of T_{ref} and T_{cell}. The number of moles of hydrogen atoms absorbed (we will simply say 'absorbed' to mean absorbed or adsorbed) or desorbed by the sample in the kth step, Δn_H^k, is then calculated from the change in the pressure measured when S is opened:

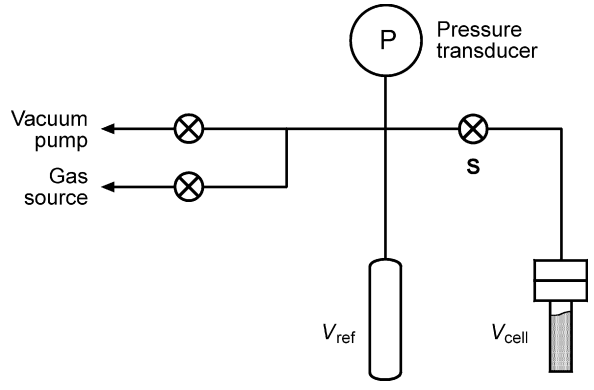

Fig. 1. Minimal Sieverts apparatus for determining the uptake of gas atoms or molecules by the sample contained in a cell with empty volume V_{cell}, based on the initial pressure of gas in V_{ref} and a further measurement of pressure after the valve S has been opened.

$$\Delta n_H^k = 2\left\{\left[\frac{p_{\mathrm{ref}}^k}{Z(p_{\mathrm{ref}}^k, T_{\mathrm{ref}}^k)RT_{\mathrm{ref}}^k} - \frac{p_{\mathrm{sys}}^k}{Z(p_{\mathrm{sys}}^k, T_{\mathrm{ref}}^k)RT_{\mathrm{ref}}^k}\right]V_{\mathrm{ref}} - \left[\frac{p_{\mathrm{sys}}^k}{Z(p_{\mathrm{sys}}^k, T_{\mathrm{cell}}^k)RT_{\mathrm{cell}}^k} - \frac{p_{\mathrm{sys}}^{k-1}}{Z(p_{\mathrm{sys}}^{k-1}, T_{\mathrm{cell}}^{k-1})RT_{\mathrm{cell}}^{k-1}}\right] \times \left[V_{\mathrm{cell}} - \frac{m_X(n_H^k)}{\rho_X(n_H^k)}\right]\right\}, \quad (1)$$

where Z is the compressibility of a real gas, defined by modifying the ideal gas law such that $pV/nRT = Z$ rather than one. The total change in the hydrogen content of the sample after N steps is

$$n_H^N = \sum_{k=1}^{N} \Delta n_H^k.$$

Eq. (1) simply accounts for all the gas in the system and has been written so as to expose the dependence of the calculation on the volume of sample present in the cell, $V_X = m_X/\rho_X$. Note that the mass of the sample, m_X, and its density, ρ_X, depend in general on its hydrogen content.

As the measurement relies on changes in the pressure in the system owing to absorption or desorption of hydrogen by the sample, a figure of merit which relates to the system resolution and accuracy is a helpful design parameter. Consider the evolution of the pressure in the hydrogenator during the kth step, and momentarily omit the index k for convenience. Once the connecting valve S has been opened and the ideally instantaneous change in pressure owing to the larger volume sampled by the pressure transducer has occurred, the system is isochoral (constant volume) and the number of moles of hydrogen contained as gas and in the sample is constant:

$$\frac{2}{R}p_{\mathrm{sys}}\sum_j \frac{V_j}{Z(p, T_j)T_j} + n_{\mathrm{H}} = \text{constant}, \quad (2)$$

where the sum runs over all the volumes in the hydrogenator, V_{ref} and V_{cell} in the simplest case under consideration. The change in the hydrogen content of the sample is therefore reflected in a change in the system pressure which is given, according to Eq. (2), by

$$\Delta n_H = -\frac{2}{R}\Delta p_{\mathrm{sys}}\sum_j \frac{V_j}{Z(p_{\mathrm{sys}}, T_j)T_j}.$$

Using the definition of H/X, the isochoral constraint may then be expressed in terms of the time evolution of the system pressure as the hydrogen is absorbed or desorbed during the kth step according to the kinetics of the sample:

$$p_{\mathrm{sys}}^k(t) = p_{\mathrm{sys}}^k(0) - s_k\Delta\left(\frac{H}{X}\right),$$

where $p_{sys}(0)$ is the system pressure immediately after the valve S has been opened, before any change in n_H has occurred, and $-s_k$ is the slope of the isochore for the kth step:

$$s_k = \frac{n_X R}{2\sum_j V_j / Z(p^k_{sys}, T^k_j) T^k_j}.$$

s_k indicates the sensitivity of the system to changes in H/X, as measured by changes in the system pressure, and so helps to quantify the performance of the hydrogenator.

To arrive at a figure of merit for the hydrogenator we compare s_k to the performance of the pressure transducer, P in Fig. 1. If the full-scale range of the pressure transducer is F and its relative accuracy is δ, the useable resolution of the transducer is $\delta p = \delta F$. The performance of the hydrogenator will improve as F decreases relative to the change in pressure (Δp_{sys}) accompanying a change in hydrogen content of the sample, and also as δ decreases. Therefore, we propose a figure of merit:

$$\eta = \frac{s_k}{\delta p}. \quad (3)$$

with $\eta \geq 100$ being a suitable rule of thumb for obtaining data of high quality in our experience, in the absence of errors in the volumes or sample density.

3. Effect of uncertain sample density

The premise of the Sieverts technique is that accurate values for all the parameters in Eq. (1) are known at the end of the kth step, most fundamentally the volumes that comprise the system. Eq. (1) shows that uncertain knowledge of the sample volume (via its mass and density) and cell volume affect the calculation as if an error had occurred in the calibration of the hydrogenator. If expansion accompanies absorption by the sample, the sample volume cannot be assumed to be constant. This effect needs then to be allowed for by calculation, which might not be feasible, or, preferably, by designing out the sensitivity to it.

Partially differentiating Eq. (1) with respect to density shows that (a) the effect of a change in density on the calculated hydrogen uptake depends on ρ^{-2}, confirming the increased sensitivity to low but uncertain sample densities, and (b) the dependence on the actual instantaneous conditions of p, V and Z is complicated and not amenable to analytic analysis. Simulation was therefore employed to explore the consequences of inaccurately known sample density and, for comparison, compressibility and volumes (see Section 4). Experimental isotherms measured on several sets of Sieverts apparatus were re-analysed with Eq. (1) using a range of assumptions for the density of the sample. The most significant differences between the various experimental setups were in the ratio of the reference volume, V_{ref}, to the empty volume of the sample cell, V_{cell}, and in the fraction of the cell volume actually occupied by sample.

Fig. 2 shows an isotherm measured for a sample of potassium-intercalated graphite with nominal density 2.0 g/cc. Varying the assumed density by ±25% produced alarming changes ~100% in the apparent quantity of adsorbed hydrogen. Given the difficulty in defining the meaning of density for this low-dimensional system, the measurements are rendered meaningless. While high pressures were applied, the error in the apparent quantity of absorbed hydrogen was already extreme at a few tens of bar hydrogen pressure.

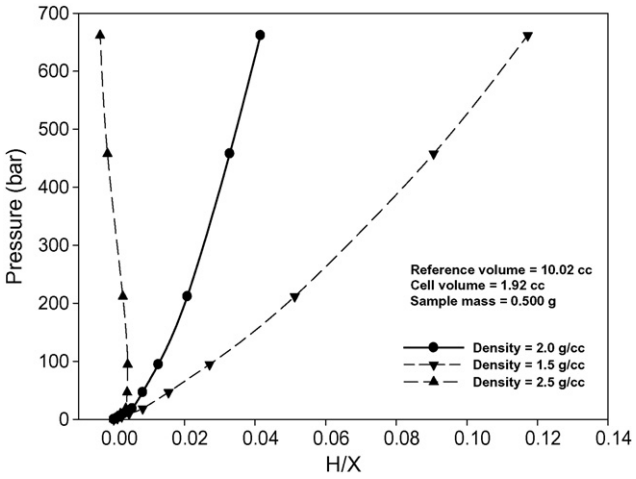

Fig. 2. Effect of a ±25% change in sample density on the apparent hydrogen uptake of $C_{24}K$ at room temperature, measured in a system of insufficient volume relative to the volume of sample.

Fig. 3 shows an isotherm measured for a sample of multi-walled carbon nanotubes with nominal density 1.5 g/cc in a second Sieverts apparatus. The apparent quantity of absorbed hydrogen owing to a ±25% variation in assumed sample density is moderate at ~10%.

Fig. 4 shows an isotherm measured with a third Sieverts apparatus for a sample of lithium nitride at 285 °C with nominal density 1.294 g/cc, calculated from the lattice parameters at room temperature [5]. In this case the amount of apparent hydrogen absorption changes by only ~0.1% in response to a change in the assumed density of to a change in the assumed density of ±25%, despite having the lowest sample density of those studied.

Fig. 5 shows an isotherm for the $LaNi_5$-H_2 system and reinforces the occurrence of the problem only among samples of low

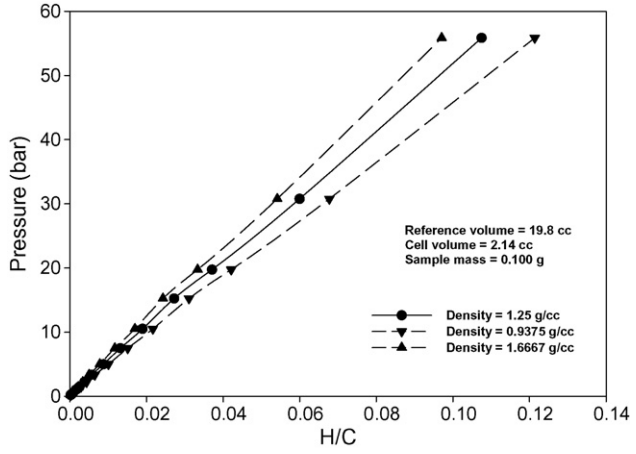

Fig. 3. Effect of a ±25% change in sample density on the apparent hydrogen uptake of a sample of carbon nanotubes at room temperature, measured in a system which is fairly large compared to the volume of sample.

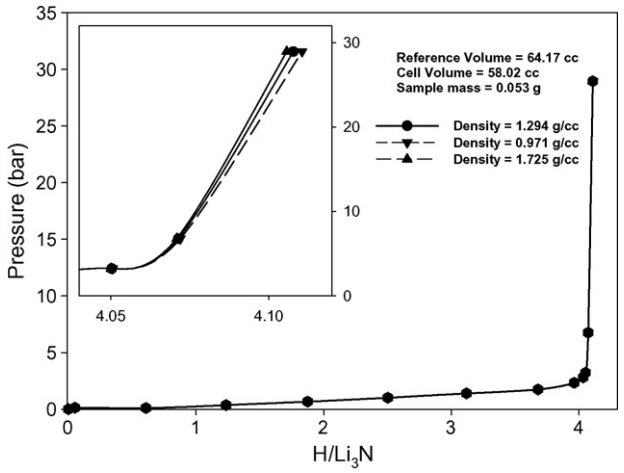

Fig. 4. Effect of a ±25% change in sample density on the apparent hydrogen uptake of a sample of Li_3N at 285 °C, measured in a system which is very large compared to the volume of sample and has comparable reference and empty-cell volumes, V_{ref} and V_{cell} in Eq. (1).

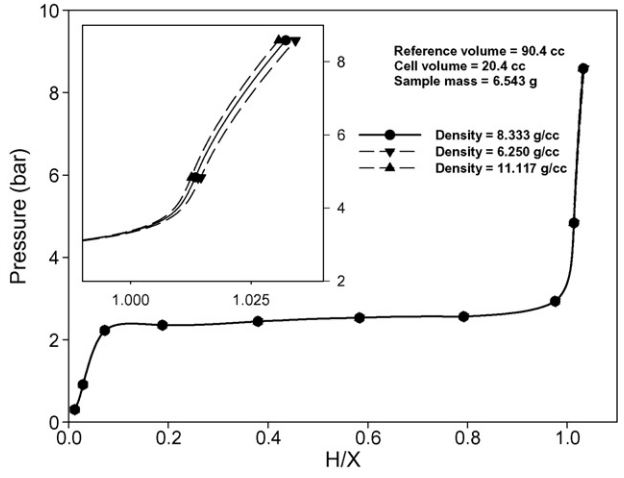

Fig. 5. Absorption isotherm of a relatively dense sample, $LaNi_5$. Note the insensitivity of the result to variations in the sample density, even though the ratio of the system volume to the cell volume is about the same as in Fig. 2.

density. Here the ratio of system to cell volume is similar to the worst case shown in Fig. 2, but the sample density is higher and the volume occupied by the sample is relatively smaller, leading to an acceptable error ~0.2% in the quantity of H absorbed when the 24% expansion of the hydride relative to the metal is ignored altogether.

4. Discussion

One's first intuition that insensitivity to the sample density will be conferred by making the sample cell volume a small fraction of the system volume is wrong. Table 1 summarises the findings of the simulation experiment. Just shrinking the cell volume does not achieve the desired outcome. Likewise, a small sample in a cell which is itself a small fraction of the total system volume is not completely effective (Fig. 3). The best outcome was obtained with comparable reference and cell volumes and a sample which occupied a small fraction of the

Table 1
Comparison of the sensitivity of the calculated hydrogen-to-host atomic ratio to a change in the assumed density of the sample, for three examples of low-density materials studied with sets of Sieverts apparatus with varying ratios of the system, cell and sample volumes

V_{sys}/V_{cell}	6.2	10.3	2.1
V_{sys}/V_{sam}	47.8	273.7	2978
V_{cell}/V_{sam}	7.7	26.7	1393
Sensitivity to density	High	Moderate	Low
η	100 approx.	150 approx.	85 approx.
Refers to figure	2	3	4

η is the figure of merit for the usable sensitivity of the Sieverts apparatus defined in Eq. (3).

system volume (Fig. 4). This may be rationalised as follows. The vulnerability of the Sieverts technique is that it relies on calculating the quantity of hydrogen exchanged with the sample in the kth step by the subtraction of two relatively large numbers, which are the amounts of hydrogen in the system before and after the kth step. If the cell volume is very small, the system pressure, p^k_{sys} in Eq. (1), will not be much different from the pressure in the reference volume, p^k_{ref}, that initiated it. If V_{ref} is fairly large, the first term in Eq. (1) will then be of moderate magnitude. However, the change in system pressure between the kth and $(k+1)$th steps may be large if the isotherm contains a small number of points, and this difference amplifies the volume term containing the difference between the empty-cell and the sample volumes, making it also of moderate magnitude. Thus there is the potential for a large effect on the calculated quantity of hydrogen exchanged with the sample owing to an error in the volume occupied by the sample, implicating the sample density.

The approach of making both V_{ref} and V_{cell} large compared to the notional volume of sample needs to be balanced against the figure of merit for the system (Eq. (3)), which will degrade as the system volume becomes too large unless a pressure transducer of increased accuracy is employed. Considering Fig. 4, we note that the total quantity of absorbed H is larger than expected from the limiting Li_3NH_4 stoichiometry by some 2.5%. The limitation on the accuracy of this measurement is most likely the marginal sensitivity of the system ($\eta < 100$), which exposes the results to systematic errors in the pressure readings. It is not possible to precisely define the optimum ratio of volumes because of the complicated dependence of the systematic error in H/X caused by a density error on p, T and Z: there is no single setup that is optimum for all conditions of pressure and temperature, but it is certainly possible to greatly lessen the sensitivity of the results to uncertain sample density by following the rules-of-thumb proposed here.

A common approach to the problem of defining the volume of the sample is to measure the effective volume of the loaded sample cell with an inert gas. The validity of this procedure is undoubted where the sample has a three-dimensional morphology and its density does not change owing to hydrogen absorption. Particularly in the case of the latter reality, however, the problem of uncertain density is still present and the system should be designed to minimise its effect. Furthermore, even He

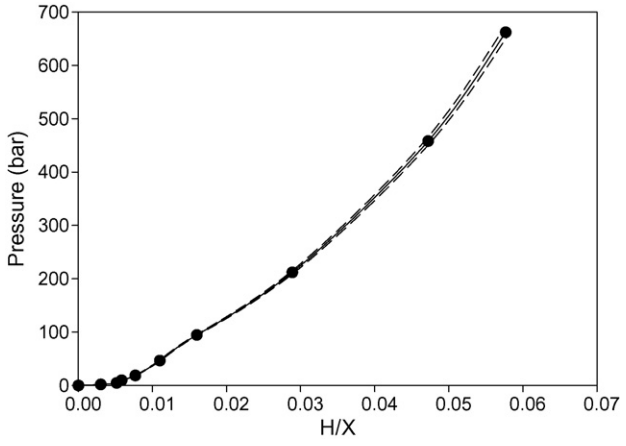

Fig. 6. Effect of a ±1% change in compressibility on the isotherm in Fig. 2. The spread of values is indicated by the dashed lines. Note the insensitivity to compressibility and, therefore temperature and pressure accuracy, relative to sample density.

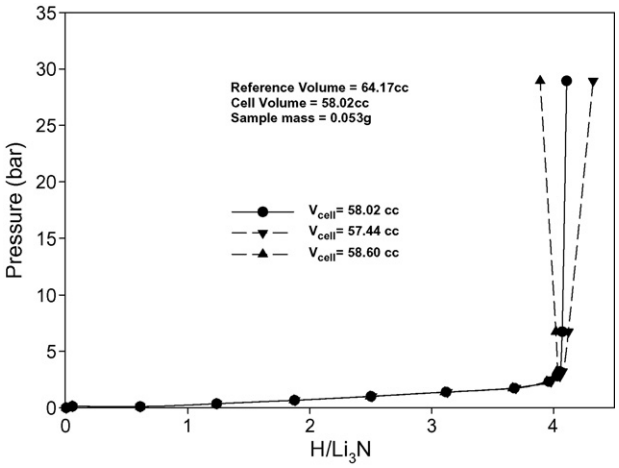

Fig. 7. Effect of a ±1% change in sample cell volume on the isotherm in Fig. 4, illustrating the necessity to accurately calibrate V_{cell} with respect to V_{ref}.

is reported to adsorb onto activated carbon and zeolites [6] and onto single-walled carbon nanotubes [7] at 300 °C, raising serious doubts about the accuracy of this approach unless great care is taken with the determination of the so-called helium density of the sample.

Comparing Figs. 2 and 5 (roughly equivalent setups) exposes the flaw in a popular method of checking the performance of a Sieverts system, that of first measuring $LaNi_5$ as a de-facto standard. As its density is high, an accurate determination of hydrogen content may well be made on $LaNi_5$, but this does not guarantee a good result with samples of low density.

Recent papers [7,8] advocate a modified Sieverts technique based on the pressure difference between identical reference and sample arms. In our view this approach, while achieving high sensitivity, is still vulnerable to systematic errors caused by uncertain sample density, as the results were shown to depend strongly on calibration of the effective volume of the loaded sample cell. The verification of performance made using $LaNi_5$ in Ref. [8] is therefore not conclusive, for the reason given above.

Lastly, we compare the effect of uncertainty in the sample density to the effect of uncertainties in the measured or calculated parameters p, T and Z and in the relative volumes of the sample cell (V_{cell}) and the reference volume (V_{ref}). As Eq. (1) depends on the first power of p, T and Z, uncertainties in their values affect the calculation in essentially the same way. Fig. 6 shows the effect on the isotherm in Fig. 2 of a ±1% change in all the values of Z in Eq. (1), representing a realistic systematic error in the compressibility. Z was calculated using a modified van der Waals equation [9] which was solved numerically [10] with accuracy better than 0.1% in the range of our data. As the effect of uncertain Z is very small compared to the effect of the ±25% assumed uncertainty in sample density, this comparison demonstrates that the density problem is very significant compared to the likely uncertainties in p, T and Z, which should all be kept small compared to 1% by design anyway to ensure high-quality results. Regarding the effect of an inaccurate volume calibration [4], inspection of Eq. (1) shows that the change in H/X in every step depends on the absolute reference volume in the same linear way. As the calibration of absolute volumes is easy to perform to an accuracy better than 1%, this is a minor effect compared to the density problem in a poorly designed system. In contrast, Eq. (1) also shows that the results have the same sensitivity to the empty-cell volume, V_{cell}, as to the volume occupied by the sample. While increasing V_{cell} to be comparable to V_{ref} mitigates the sample density problem, it consequently becomes important to carefully calibrate V_{cell} against V_{ref} to maintain accuracy. Fig. 7 shows the effect on the isotherm in Fig. 4 of a 1% error in V_{cell} with V_{ref} held constant. The ratio $V_{cell}//V_{ref}$ must therefore be determined as accurately as the uncertainties in p, T and Z allow.

5. Conclusions

By simulating the effect of unknown or wrong density for samples of low density in several sets of Sieverts apparatus, we have developed rules-of-thumb for designing a system which limit the effect of the density uncertainty on the calculated quantity of hydrogen in the sample. These rules are (i) ensure that the reference volume and the empty-cell volume are (a) both large compared to the volume notionally occupied by the sample, by a factor of at least 100 in each case, and (b) ideally about equal; (ii) ensure a figure of merit for the hydrogenator (Eq. (3)) of at least 100. Demonstrating accurate results with a relatively dense "standard" sample such as $LaNi_5$ does not guarantee accuracy with low-density samples. In a poorly designed system the density problem may be much more significant than feasible errors in system variables or volume calibrations. System variables (p, T, Z) should be determined with accuracy significantly better than 0.1%. The ratio of the sample cell volume to the reference volume should be calibrated to better than 0.1%.

Acknowledgement

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