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Pitfalls in the characterisation of the hydrogen sorption properties of materials

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D.P. Broom [a,*], C.J. Webb [b]

[a] Hiden Isochema Ltd, 422, Europa Boulevard, Warrington WA5 7TS, UK
[b] Queensland Micro- and Nanotechnology Centre, Griffith University, Brisbane, Australia

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ABSTRACT

Characterising the hydrogen sorption properties of materials is important for a range of applications, including solid state hydrogen storage, electrochemical and thermal energy storage using metal hydrides, and H_2 gas compression and purification. However, it can be technically demanding and subject to significant error if not performed with care. In this article, potential pitfalls in the performance of hydrogen sorption measurements are discussed. The topics covered include instrument design and calibration, sample size choice, sample and gas purity, isotherm measurement procedure and issues associated with data reduction. Approaches to validating equipment and isotherm measurements are also discussed. Different sample types are considered, including metal and complex hydrides and nanoporous adsorbents, such as porous carbons, zeolites and metal-organic frameworks (MOFs).

Contents

Introduction

Accurately determining the hydrogen sorption properties of materials is critical to assessing their use in a range of applications, but it is also required for fundamental studies. Hydrogen absorption by elemental metals, alloys and intermetallics [1–7] has been of interest ever since the reversible absorption of hydrogen by Pd was first discovered, over 150 years ago [8]. However, more recently, the uptake and release of hydrogen by a range of other materials has been studied, including complex hydrides [9,10], such as sodium alanate [11], borohydrides [12–14] and the Li-N-H system [15,16], non-porous polymers [17–19], and nanoporous materials that include porous carbons [20–22], zeolites [23], metal-organic frameworks [24–26] and microporous organic polymers [27–29].

Much of the recent work has been driven by the intense interest in mobile hydrogen storage [30–35]. As a result, most of the above materials have been considered for this purpose [9,10,33,36–39]. However, metal hydrides have many other applications, including electrochemical [40,41] and thermal energy storage [42,43], in actuators [44] and heat switches [45,46], compressors [47,48], heat pumps and cryocoolers [49], as getters [50–53], and for isotope (H_2/D_2) separation and H_2 purification [36,54–56]. To date, the most commercially

successful of these is the use of $LaNi_5$-based materials in Ni-MH (Nickel-Metal Hydride) battery electrodes [57–59], but research into new materials for this application is being actively pursued [41,60]. Meanwhile, traditional nanoporous materials, such as activated carbons and zeolites, are commonly used to separate and purify H_2 using pressure swing adsorption (PSA) [61]. Polymeric membranes are also widely used in separations involving H_2, including ammonia purge gas recovery, refinery gas purification and syngas ratio adjustment [17,62]. These processes rely on H_2 separation from N_2, CH_4 and CO, respectively [62]. Such membranes are also among the many types being investigated for H_2 purification for fuel cell applications [56,63], while isotope (H_2/D_2) separation is an emerging H_2 sorption-based application for nanoporous materials [64–68].

Different applications require different hydrogen sorption properties [3,36,54,55]. For example, for H_2 storage, a significant amount of reversible uptake must occur at above ambient pressures due to delivery pressure demands. In contrast, battery electrode materials must reversibly absorb hydrogen at sub-ambient pressures because of the operating conditions of electrochemical cells [3,57]. When metal hydrides are used to compress H_2 gas to pressures of tens of MPa, materials with reversible capacities at these higher pressures are required [47]. At the other end of the scale, for getters, absorption must occur at very low, sub-mbar, pressures

[50–53]. Operating temperature is also important, with some applications, such as thermal energy storage [42], requiring absorption and desorption to occur at much higher temperatures than the near-ambient conditions needed, for example, for mobile H_2 storage. Overviews of specific requirements for metal hydrides for different applications can be found in a number of articles [36,54,55], while more detail is provided in reviews on particular applications, such as H_2 compression [47] and separation [56] and thermal energy storage [42]. In each case, it is clear that the H_2 sorption properties of candidate materials must be characterised to sufficient accuracy.

The starting point, regardless of application, is often the determination of sorption isotherms, which are plots of H_2 uptake against pressure at fixed temperature. Individual isotherms provide basic capacity information; for example, for H_2 storage, an isotherm measured at the operating temperature of the store gives both the maximum capacity of a material and its reversible capacity between a minimum and maximum operating pressure. However, measurement of isotherms at a series of temperatures also enables determination of the thermodynamics of the interaction of H_2 with the material using the van't Hoff relation [36,55,57]. This allows calculation of the changes in enthalpy and entropy for hydride formation or decomposition, for metal hydrides, or the isosteric enthalpy and entropy of H_2 adsorption for nanoporous materials [69]. Such thermodynamic information is of interest for both fundamental reasons and for practical applications. In addition, isotherm shape at different temperatures can also be important. For example, for H_2 compression, sloping plateaus in metal hydride pressure-composition isotherms can lead to lower compression ratios, for a given pair of upper and lower operating temperatures [47].

Hydrogen sorption measurements can, however, be technically demanding and subject to a number of sources of experimental error [35,70–87]. This has been demonstrated by a number of high profile controversies in hydrogen storage material research [88], the most prominent of which was over the storage properties of carbon nanostructures. In this case, in the late 1990s, high storage capacities were reported by a number of authors [89–92] but the results were later shown to be irreproducible, as summarised recently by Broom and Hirscher [88]. Further problems, however, have occurred with data reported for boron nitride nanotubes, conducting polymers, metal-organic frameworks (MOFs) and various materials purported to store large amounts of hydrogen via spillover [88]. The latest controversy involves hydrogen storage in graphene-based materials [93].

The problems described above led to recent interlaboratory exercises, which found a disturbing disparity between the results reported by the participants [94,95]. Zlotea et al. [94] reported the H_2 adsorption properties of a commercial porous carbon at 77 K and ambient temperature, at pressures up to 10 MPa and 20 MPa, respectively, while Moretto et al. [95] reported the hydrogen absorption and desorption properties of a MgH$_2$-based material at temperatures of 553 K and 593 K. Results from these studies are shown in Figs. 1 and 2, in which the disparity, particularly at higher pressures, is clearly evident. Possible reasons for this are discussed in more detail later, but the variation in data found for different types of
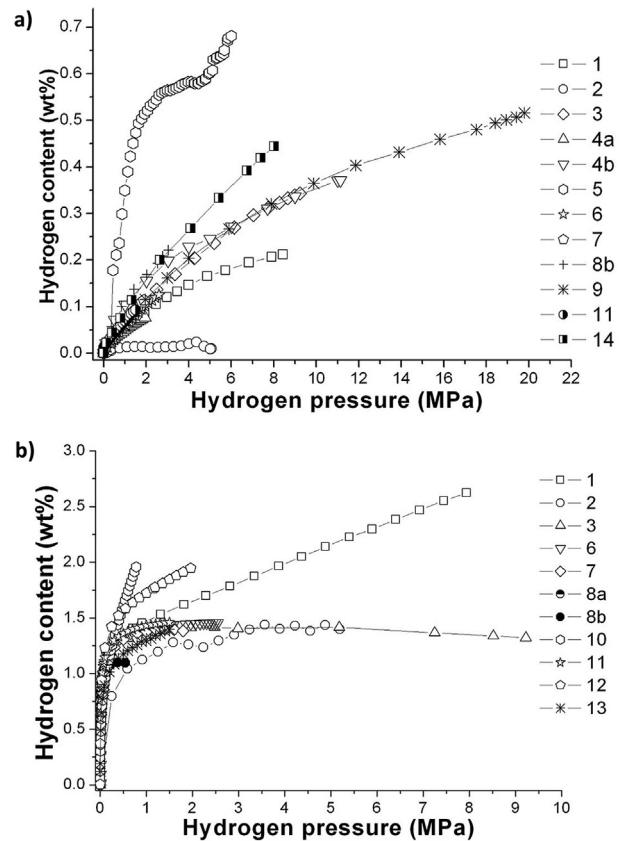
Fig. 1 – Hydrogen adsorption data for the porous carbon Takeda CMS 4A, measured at (a) ambient temperature and (b) 77 K in different European laboratories [94]. (Reprinted from International Journal of Hydrogen Energy, 34(7), C. Zlotea et al., A Round Robin characterisation of the hydrogen sorption properties of a carbon based material, 3044–3057, Copyright (2009), with permission from Elsevier).

material illustrates the susceptibility of hydrogen sorption measurements to error, and suggests this is a more general problem.

This article therefore discusses the potential pitfalls encountered when characterising the hydrogen sorption properties of materials. We begin by introducing the most common measurement methods, before covering pitfalls in the main section and then concluding with a discussion.

Sorption measurement techniques

The hydrogen sorption properties of materials are typically determined using either manometric or gravimetric techniques. Each approach allows quantification of hydrogen uptake as a function of both temperature and pressure.

Manometric technique

In the manometric case, also known as the volumetric or Sieverts technique, measurement of H_2 pressure and
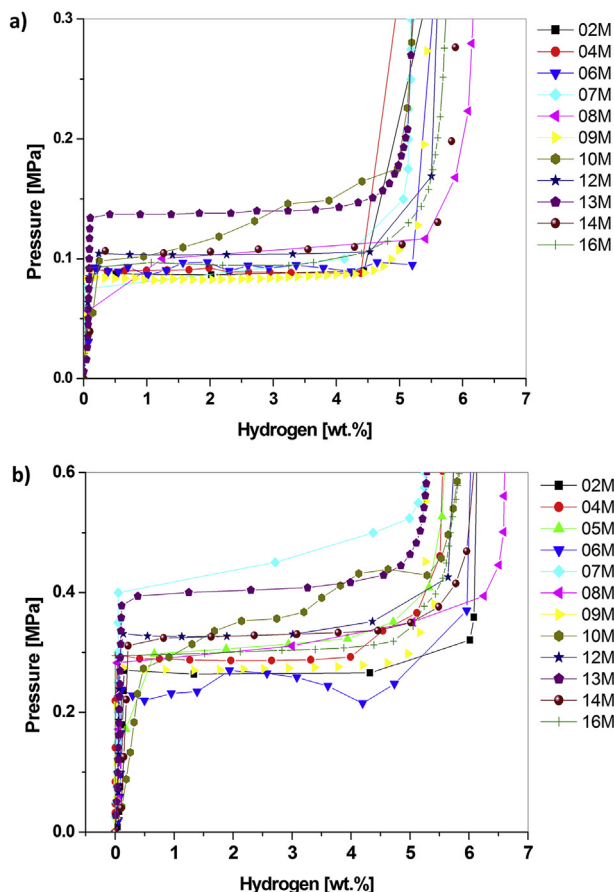
Fig. 2 – **Hydrogen absorption data for a doped MgH$_2$ sample measured at (a) 553 K and (b) 593 K in different laboratories [95]. (Reprinted from International Journal of Hydrogen Energy, 38(16), P. Moretto et al., A Round Robin Test exercise on hydrogen absorption/desorption properties of a magnesium hydride based material, 6704–6717, Copyright (2013), with permission from Elsevier).**

Fig. 3 – **Schematic diagrams of (a) a simplified manometric apparatus [79] and (b) gravimetric apparatus employing a symmetric microbalance with both the sample (S) and the tare weight (T) suspended in the gas [87]. (Reprinted from Journal of Alloys and Compounds, 446–447, T. P. Blach, E. M. Gray, Sieverts apparatus and methodology for accurate determination of hydrogen uptake by light-atom hosts, 692–697, Copyright (2007), and International Journal of Hydrogen Energy, 39(13), C. J. Webb, E. M. Gray, Analysis of uncertainties in gas uptake measurements using the gravimetric method, 7158–7164, Copyright (2014), with permission from Elsevier).**

temperature, combined with an equation of state for H$_2$ and the volume of the apparatus, is used to determine the quantity sorbed (absorbed or adsorbed) by a material [35,79–81,85,96–98]. Fig. 3(a) shows a simplified manometric apparatus. The instrument consists of two fixed volumes coupled by a valve – a reference or dosing volume and a sample cell. A pressure transducer is mounted on the reference volume and temperature sensors (not shown) measure the temperatures of both volumes. More sensors are required when different parts of the apparatus are subject to different temperatures, and different transducers ca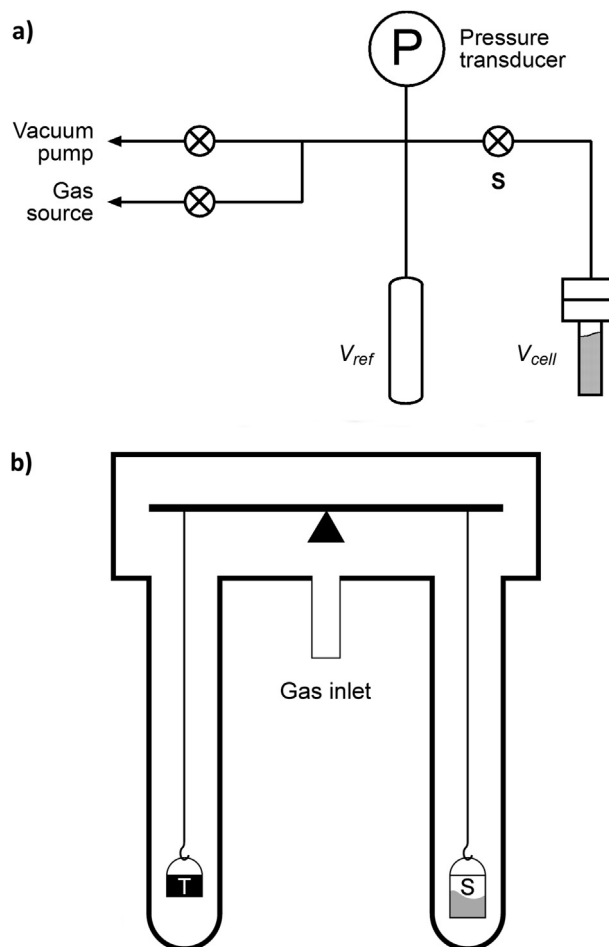n be used to cover different pressure ranges. Initially, a specific amount of material is loaded into the sample cell and all volumes are evacuated. Some sample preparation is often required, for example, heating under vacuum to remove moisture, oxygen or other contaminants, such as solvents remaining from the synthesis process.

An isotherm measurement usually begins with evacuation of the sample cell at the required temperature. This provides a

reference point for the uptake calculation. A known amount of gas, calculated using the real gas law, is then prepared in the reference volume. As the process of filling this volume involves some gas expansion, adiabatic effects require thermal equilibration to be achieved before the pressure and temperature measurements can yield an accurate value for the gas quantity. After thermal equilibration, the separating valve, labelled 'S' in Fig. 3(a), is opened and gas expands into the sample cell. Adiabatic gas expansion and the exothermic or endothermic reaction of H$_2$ with the material lead to changes in temperature, while H$_2$ sorption alters the pressure. Therefore, thermal and pressure equilibrium must again be established before a reading is taken. The equilibrium pressure and temperature is then used to determine the amount of gas in

both volumes. Since the system is closed, any difference in the amount of gas can be attributed to H_2 uptake by the sample, providing the instrument is free of leaks. In this sense, manometric sorption measurements are indirect as the uptake is only inferred from pressure changes. They also rely on the assumption that no other effects contribute to the pressure difference.

The above describes the first step in an isotherm measurement, which yields a single value of H_2 uptake at a particular equilibrium pressure. To continue, the sample cell is isolated, and the reference volume prepared with a new aliquot of gas. Once the valve is again opened and a stable measurement taken, the additional increment in the uptake can be determined. The uptake following this step is then the sum of these two values. These steps continue until the maximum measurement pressure is reached. The incremental uptake values can then be summed in order to calculate the uptake at each equilibrium pressure. Detailed descriptions of this technique were provided by Gray [81] and Broom [35].

Gravimetric technique

In comparison, the gravimetric technique typically uses a microbalance to directly measure the change in sample weight due to H_2 sorption [35,80,81,87,99,100]. The balance may be single or doubled-sided [81]. In the latter case, a tare weight is normally applied to the opposing side (Fig. 3(b)). The sample is placed in a holder attached to one side of the balance and any sample preparation procedures performed. A measurement begins with the sample under vacuum at the desired temperature. A pressure of H_2 is introduced to the microbalance chamber; any interaction between H_2 and the material changes the measured weight. Once the balance signal has stabilised, a weight reading is taken, which provides the first isotherm point. To measure the next point, the H_2 pressure in the chamber is increased and another weight reading taken. This continues until a full isotherm has been determined. Gravimetric measurements are direct, as the increase in sample weight due to hydrogen uptake is measured directly by the balance; however, the weight readings must be corrected for the buoyancy of both the sample and any other components attached to the balance [35,81,87].

Although it requires more expensive instrumentation, the gravimetric technique has the advantage that the internal volume of the instrument is not used to calculate the uptake. At any pressure, the amount of H_2 sorbed by the sample is instead given by the (corrected) balance reading, referenced to the sample mass under vacuum. Another advantage is therefore that a sorption measurement at a specific pressure is independent of any previous uptake measurements, unlike the manometric case. This significantly reduces the uncertainty in the final uptake value at the highest equilibrium pressure [87]. A further benefit, in contrast to manometric measurement, is that isobars can readily be determined by changing the sample temperature under constant pressure conditions [99]. Further details regarding the gravimetric technique were provided by Gray [81] and Broom [35].

Measurement pitfalls

In principle, both techniques are straightforward as they simply involve measuring pressure, temperature and sample weight; combined with knowledge of the system volume, in the manometric case. Yet this apparent simplicity is deceptive. Small errors in some parameters can lead to large errors in the calculated uptake, the magnitude of which increases significantly under certain conditions in ways that may not be immediately obvious. For example, manometric measurement, at near ambient temperatures and pressures, of hydrogen absorption by $LaNi_5$, a hydriding intermetallic with a high bulk density, is relatively immune to errors that, in contrast, can greatly affect high pressure measurements of H_2 adsorption by a (low density) nanoporous material at 77 K.

Errors affecting hydrogen uptake measurements have been widely discussed for years [70,71,73,75−78,101−110]. However, the main sources were categorised in 2007 by Broom [80], in the context of the accuracy of hydrogen storage material characterisation. Some of these were also under more rigorous analysis around the same time [79]. Since then, a United States (US) Department of Energy (DOE) project has defined best practices in the characterisation of the hydrogen storage properties of materials [111] and, in 2011, a book covering the main experimental considerations in hydrogen sorption measurement was published [35]. Further work has continued on various aspects of measurement accuracy [83−87] but an explanation of the most significant practical problems encountered when performing hydrogen sorption measurements, regardless of the intended application or material, is missing from the literature. This article aims to fill this gap. In this section, we therefore discuss the main pitfalls.

Instrument specifications

For optimal results, instruments are best designed with the nature of the sample and application in mind. Heterogeneous materials, for example, may require a large sample cell to contain sufficient sample to average over the inhomogeneities. In contrast, novel nanoscale compounds may only be available in small quantities. Also, as noted in the Introduction, different applications require different pressure regimes, together with different experimental temperatures. Tailoring instruments to specific samples or applications, however, is often not feasible, as they are typically purchased from a limited set of configurations or designed intentionally for flexibility. The limitations of each instrument must therefore be accommodated during measurements. If a fixed configuration is used − a commercially supplied apparatus, for example − it is important to consider whether it can make accurate measurements on a material in the quantities available.

Manometric instruments
Manometric measurements rely on differences in the amount of gas contributing to the pressure before and after the sample is exposed to H_2; so a small H_2 uptake results in a significant relative uncertainty. The more gas involved in the measurement − for the same sample size and uptake − the greater that

uncertainty. Hence, larger reference and sample cell volumes are more likely to lead to inaccurate calculations [84]. In addition, each measurement step involves gas expansion from the reference volume into the combined reference and sample cell volume so the ratio of these volumes is also important. When the sample cell and dosing volume temperatures are similar, as is typically the case for near ambient temperature measurements, the best results are obtained with approximately equal volumes [79,85].[1] However, at lower sample temperatures —77 K, for example — it is better for the volume ratio to more closely match the ratio of the temperatures of the reference volume and sample cell [114], resulting in a larger reference volume. Also, to calculate uptake, the quantities of gas in the individual volumes are determined from pressure and temperature. Accurate sorption measurements thus require high accuracy transducers and sensors that are carefully calibrated, together with knowledge of the internal volumes (see Section Instrument calibration).

The critical specifications of a manometric instrument are therefore the absolute values of the reference and sample cell volumes, the ratio of these volumes, and the accuracy of the pressure and temperature measurement and volume calibrations. In addition, any manometric system must also be leak tight.

Gravimetric instruments

In contrast, the internal volume of a gravimetric instrument does not need to be known because the sorbed weight is measured directly. However, each microbalance has a resolution, specifying the minimum measurable weight change and hence the minimum measurable H_2 uptake. Resolution is practically limited by long term stability, which depends critically on the thermal and mechanical stability of the microbalance enclosure [35]. High sensitivity balances can have a quoted resolution of 0.1 μg, but a long term stability of this level is difficult to achieve. Also, higher resolution instruments are more delicate. This can limit maximum capacity, which in turn limits the amount of sample that can be used. For a single-sided balance, this is the maximum weight that can be applied and measured, but for double-sided balances the specifications may quote maximum applied weights for both the tare and sample sides, as well as a maximum differential weight, or weighing range.

The critical specifications of a gravimetric instrument are therefore the resolution and long term stability of the microbalance, its maximum weighing capacity and, for double-sided balances, the maximum weights that can be applied to either side. However, the accuracy of the pressure transducers can limit the range of pressures over which accurate sorption isotherms can be determined.

Pressure measurement

Pressure measurement is required for the gravimetric method in order to define the measurement conditions and to calculate buoyancy forces. However, for manometric

measurements it is used directly to calculate H_2 uptake. It is therefore more significant to the uncertainty in calculated uptake [85], and hence its resolution — the minimum uptake that can be reliably measured at any step.

Pressure transducers based on crystal oscillator sensors typically have accuracies expressed as a percentage of full scale range (FSR). The product of this quoted percentage accuracy and the FSR gives the absolute accuracy, and this is constant for all measurements. The relative accuracy, however, is greatest at the maximum pressure and poorer at lower pressures. For example, for a 10 MPa transducer with an accuracy of 0.02% FSR, the absolute accuracy is 2 kPa but the relative value at 0.1 MPa is 2%. A 200 MPa transducer with an accuracy of 0.02% FSR, meanwhile, has an absolute accuracy of 40 kPa. The relative uncertainty at 0.1 MPa is therefore 40%, prohibiting accurate manometric sorption measurements at this pressure.

Capacitance manometers, on the other hand, often have an accuracy quoted as a percentage of reading. Typical percentage accuracies for these sensors are poorer — for example, 1% of reading [111] — but they offer the potential advantage of higher absolute accuracies at lower measurement pressures. However, there is a trade-off because of their lower accuracy at higher pressures.

Nevertheless, attempting to measure H_2 uptake at low pressures compared to the range of the transducer is a significant pitfall. Selecting the lowest range transducer for a chosen application provides the highest H_2 sorption measurement accuracy, bearing in mind that systems can be fitted with transducers covering different ranges [97]. Furthermore, at very low pressures, for example <100 Pa, thermal transpiration corrections are necessary if a temperature difference exists between the transducer and the sample cell [35,80,103,113,115]. Rouquerol et al. [116] noted, with regard to adsorption measurements at 77 K, that an error of nearly 100% in the pressure reading is possible if thermal transpiration is ignored.

Temperature measurement

Temperature sensors are readily available for a wide range of measurement conditions [117]. Thermocouples with typical absolute accuracies of ±1 K and platinum resistance thermometers (PRTs) with typical accuracies of ±0.1 K, for example, can be obtained at reasonable cost, with different sensors appropriate to different ranges. At 300 K, the accuracy of a measurement using a PRT is approximately ±0.03%, but this percentage increases for lower temperatures; for example, at 77 K, a typical measurement temperature for nanoporous adsorbents, it becomes ±0.13% — assuming the absolute accuracy in this range is independent of temperature. This leads to a greater contribution to H_2 sorption measurement uncertainty at lower temperatures.

When measuring pressure, it is often unnecessary to use more than one transducer because pressure will equalise rapidly following any change — assuming there are no apertures small enough to significantly limit gas flow. In contrast, the temperature of different parts of the apparatus may differ significantly and readings can be slow to stabilise [84], so multiple sensors are often required. For manometric measurements, in particular, accurate knowledge of gas

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[1] This was also shown to be the case for N_2 sorption by polymers by Koros and Paul [112], and was recommended by Ross and Olivier [113] in their earlier discussion of gas adsorption measurement.

temperature in each volume is crucial to accurately calculate gas quantities. A pitfall in the design of a manometric instrument is therefore the inability to accurately determine all relevant gas temperatures throughout the system. This may be due to temperature fluctuations, an insufficient number of sensors in the gas phase, or their location at a distance from the majority of the gas volume; for example, on the outside of pressure vessels or tubing. Minimising the amount of unthermostatted volume in any manometric system is also beneficial, as any ambient temperature fluctuations will contribute to measurement uncertainty, regardless of the accuracy of temperature measurement or control in other parts of the apparatus. Typical materials used for valves and tubing (stainless steels) have poor thermal conductivity compared to some other metals so this may exacerbate the problem.

Vacuum pump selection

The achievable base pressure in a sorption system is limited by the type of vacuum pump. Different vacuum levels can be classified as *low vacuum* (10^5 to 10^2 Pa), *medium vacuum* (10^2 to 10^{-1} Pa), *high vacuum* (10^{-1} to 10^{-6} Pa), and *ultra-high vacuum* (10^{-6} to 10^{-10} Pa) [118], although the definitions can vary [119]. Different base pressures are required for different material types and for measurements made under differing conditions. Important considerations include the lowest measurement pressure needed for the material being studied, or its intended application, and the required degassing or activation conditions. Studies on materials that absorb or adsorb H_2 at low pressures require a low enough base pressure for an accurate sorption measurement to be made, without the interference of impurities, while nanoporous materials often need high vacuum conditions to initially remove pre-adsorbed contaminants from micropores [120]. Different types of pump provide different base pressures, but the vacuum achieved at the sample position also depends on the tortuosity of the pumping path and the quality of the seals in the system [35]. Furthermore, removing adsorbed species, such as water, from the internal surfaces of an instrument may require heating to reach the lowest pressures (see, for example, discussion of the baking of vacuum systems in O'Hanlon [119]). This is particularly important when making measurements at low pressures.

In many cases, a high vacuum pump system is required. Such systems include turbomolecular and diffusion pumps, while medium vacuum conditions can be achieved using rotary vane, scroll or diaphragm pumps, which are also effective as backing or roughing pumps [119]. Diffusion and rotary vane pumps, however, use oil, which can result in backstreaming of hydrocarbon vapours and hence contamination of the sorption system. Such contaminants can adsorb to samples, causing measurement errors, or they may react with the surface [121,122], altering the hydrogen sorption behaviour of the material. Using a dry pump system — for example, a turbomolecular pump backed by a diaphragm pump — is therefore advantageous.

If above-ambient pressure H_2 sorption measurements are a priority and low or medium vacuum conditions allow activation of the sample, then a rotary, scroll or diaphragm pump may suffice. When using a rotary vane pump, however, a foreline trap is generally necessary to minimise contamination.

Construction materials and component compatibility

Choice of construction material for a system depends to a certain extent on the required measurement conditions [123]. At high pressures and temperatures, for example, some materials are susceptible to hydrogen permeation [124,125], which can lead to measurement error. Another consideration is hydrogen embrittlement and attack [126–129]. Hydrogen embrittlement tends to occur at near ambient temperatures [127], whereas hydrogen attack occurs at elevated temperatures [126,128]. With regard to hydrogen embrittlement, information on the suitability of materials for use with high pressure H_2 is available in the literature [130]. However, off-the-shelf components suitable for high pressure H_2 operation are usually constructed from 316 L stainless steel, which offers good performance over a range of pressures and temperatures, but with upper temperature limitations. Hydrogen permeation resistant surface coatings can be used for higher temperature operation (see, for example, the discussion in Ward et al. [43]).

With regard to component selection, manometric instruments must be leak free, which can be a particular problem for H_2. Leakage leads to measurement errors in the manometric case, as noted by a number of authors [73,75,77,78], but it is also a safety issue. Thorough leak testing of equipment is therefore important. In addition, for both techniques, contaminant ingress through outboard leaks is possible, particularly under high vacuum conditions. High performance components are thus required, preferably with all-metal seals [35], such as VCR, or metal cone-to-cone seals such as Sitec, Nova Swiss and Maximator high pressure components, as they are compatible with both high vacuum and high pressure operation; while fittings featuring elastomer seals can be susceptible to leaks at higher pressures. For high vacuum operation, if high pressures are not required, standard Ultra-High Vacuum (UHV) components, such as Conflat (CF) flanges, are another option. It is also necessary for measurement devices, such as temperature sensors and pressure transducers, to be suitable for use with H_2. This can involve the coating of temperature sensor sheaths and transducer membranes.

Instrument calibration

Calibrating a measuring device involves ensuring the measured value equals the true value within the expected uncertainty; that is, ensuring the measurement is accurate. This typically requires comparison of the output to a sufficiently accurate standard device or a standard process or system. In this section, we consider calibration of temperature, pressure and weight measurement, accurate determination of volume in both manometric and gravimetric systems, and validation of the operation of both instrument types.

Temperature, pressure and weight calibration

Temperature calibration can be performed either by comparison to a calibrated temperature sensor or by immersing a

sensor in fluids for which the temperature is well known at fixed points, such as the triple, boiling or freezing points of N_2, water, metals and different oils [117,131]. A mathematical function, typically a polynomial, is then used to determine the temperature from the actual measurement (voltage, resistance or uncalibrated temperature) [117]. Pressure transducers can likewise be calibrated against a previously calibrated transducer or by using a dead-weight tester, which determines pressure from weights acting on a piston [132]. For gravimetric systems, the balance itself can be calibrated using standard weights [100]. The output of measurement devices can drift with time, so a significant pitfall is failure to maintain calibration of all devices in a sorption instrument.

Volume calibration for manometric instruments
The internal volumes of a manometric instrument must be accurately determined using an appropriate method. Typically, gas is expanded from a calibrated volume into an unknown volume [35,97], or it is expanded from one unknown volume to another both with and without a known displacement volume present [133]; the resultant set of simultaneous equations is then solved. The same technique can be implemented using a piston of known displacement [81]. Alternatively, an unknown volume can be filled with a fluid of known density at a specific temperature, typically water at room temperature, and the amount of fluid weighed or measured by a calibrated volume [134]. Each approach results in uncertainties, the contribution of which to the overall H_2 uptake uncertainty at elevated pressures can be significant [86].

Most manometric systems are not as straightforward as shown in Fig. 3(a), so they contain additional volumes in the gas handling system, which must be calibrated if they are involved in a measurement. The internal volume of valves can also differ depending on whether the valve is open or closed, so these differences must be accounted for, if they are significant compared to the total volume of the system. In such cases, careful calibration of all the measurement volumes is required.

Samples are also often held at a different temperature to other parts of the apparatus. To accurately calculate gas quantities, volume calibrations must therefore account for the differing temperatures. If individual volumes are isothermal, only knowledge of the physical volumes together with the temperatures is required. However, when different parts of one volume are at different temperatures, with a separating temperature gradient, a different calibration method is necessary. Two common techniques are the *equivalent-volume model* [81], in which the equivalent volume at ambient temperature is determined for a range of temperatures and pressures, and the *divided-volume model* [35,81], in which the temperature gradient is modelled as two discrete temperature volumes. Both approaches can correctly account for differences in real gas behaviour, as a function of temperature and pressure, as explained by Gray [81]. However, they also rely on maintaining the same conditions during the experiment as during calibration. Failing to do this invalidates the uptake calculation, as incorrect volumes are used. This is particularly important when a liquid bath, often N_2, is used for temperature control. Varying liquid levels due to evaporation or varying temperature gradients, due to ice accretion, for example, can make it difficult to operate under the same conditions, leading to errors. This is a general problem that affects all gas adsorption measurements made at 77 K using a liquid N_2 bath [135].

Volume calibration for gravimetric instruments
In a gravimetric system, the volume occupied by the gas does not need to be known; however, the volumes displaced by the components connected to the balance are required to calculate the buoyancy forces [35,81]. For a single-sided, isothermal system, the total volume of all items attached to the balance arm is required, including hangdown wires or rods and the bucket or sample holder. The part of the balance arm immersed in the gas may also contribute to the buoyancy depending on its position in relation to the pivot point. If any parts of the apparatus are at different temperatures, however, the individual volumes of all items at each temperature must be known. For a double-sided balance, the tare side buoyancy contributions must be included [35,81], although if both sides of the balance are at the same temperature, in principle, only the volume difference between the sides is required.

System validation
The accuracy of volume calibration in a manometric system, combined with calibration of the measurement devices, can be tested by measuring empty sample cell isotherms and H_2 sorption isotherms for a well-understood material [35,97,98]. Empty sample cell isotherms should show no sorption for all pressures, within the expected uncertainty based on the instrument specifications; while H_2 sorption isotherms measured for a known sample should show the expected behaviour. Using a sample exhibiting strong temperature and pressure dependence is advantageous. Any deviations can indicate poor volume calibration but the shape of the resultant isotherms may also indicate the nature of the errors [86]. A pitfall, in this case, is failure to check the accuracy of volume calibration using the above tests, prior to performing H_2 sorption measurements on the material under investigation. Unfortunately, no recognised standard materials for H_2 sorption currently exist; unlike those, for example, that are available for X-ray and neutron crystallography, such as silicon powder (e.g. NIST Standard Reference Material, SRM-640) and LaB_6 (e.g. NIST SRM 660).[2]

For gravimetric systems, buoyancy volume accuracy and measurement device calibration can also be checked by measuring an isotherm without a sample. Using denser gases, such as N_2 or Ar, amplifies the buoyancy effects because the force on any given component is increased by the larger molar mass of these species. The buoyancy correction procedure for the sample itself can be tested using a non-interacting sample of known volume, and measuring its apparent weight change as a function of pressure. Back calculation of the sample volume from the microbalance signal should yield a result in accordance with the known value. Finally, H_2 sorption measurements made on well-understood materials, as described above, provides a method to check the calibration of the

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[2] Information regarding the full range of standard reference materials (SRMs) available from NIST can be found on their website (https://www.nist.gov/srm, accessed June 2017).

microbalance, pressure transducers and temperature sensors, as well as the data processing methods.

For both techniques, obtaining agreement between results from known materials, while not guaranteeing all aspects of the instrument and technique are without error, remains the sole method by which the full range of measurement errors can be determined. It is therefore essential in any instrument calibration procedure. It is important to note that the known material should have similar characteristics, such as density, porosity and uptake, to the studied material. For example, an ambient temperature measurement on a high density inter-metallic such as $LaNi_5$ is a poor standard for validation of an instrument to be used for nanoporous materials at 77 K, as it does not adequately test the conditions to which (low density) nanoporous samples are sensitive [79,81].

Sample size

The quantity of material used to measure H_2 sorption may be limited practically by the available amount, the sample holder size or the microbalance capacity. Sample holder size can be a particular limitation for low density materials. However, regardless of practical restrictions, the amount of sample used can significantly affect the accuracy of a result, so poor sample size choice is a pitfall for all measurements.

General considerations

For a particular material in a given instrument, sample size can influence measurements in two ways. Firstly, it affects uptake measurement resolution, in terms of a specific quantity such as wt%, since the larger the sample, the higher the absolute molar H_2 uptake at the same pressure and temperature. For manometric measurements, for example, smaller samples increase the uncertainty in the calculated wt% uptake for a system of a given volume [84,85,97]. Secondly, any error in sample volume, due to inaccurate density determination, for example, increases the likelihood of errors in the sorption measurements with increasing sample size. A balance must be found between these competing effects. Unfortunately, measuring or determining the volume of a material can be deceptively complex [136]. For gas adsorption measurements on nanoporous materials, in general, this problem has led to recent work on alternative definitions of adsorption that do not require accurate knowledge of the sample volume (see Section Excess and absolute adsorption) [137–139].

In the manometric technique, the void volume — the volume in the sample cell accessible to H_2 — must be known in order to calculate H_2 uptake, using the conventional definitions. This can be experimentally determined by measuring the cell volume with the sample present using a gas, typically helium, that is not expected to interact with the sample; or by subtracting a calculated sample volume from the empty cell volume [35,81,85]. Difficulties arise when using helium because it may not access the same volume as H_2, particularly for microporous materials, and it may also adsorb [140–142]. At any given pressure, the amount of adsorption will increase with decreasing temperature. Low temperature void volume determination should therefore be avoided. As a result of these effects, some authors have advocated using elevated

temperatures for microporous materials [140,142]; but, regardless, helium volume calibration for these materials should not be performed at 77 K, as adsorption will affect the result, leading to measurement errors.

Gravimetric measurements also require sample volume as it is used to correct for buoyancy. Pycnometry can be used to measure volume *in situ* using helium or another non-interacting gas but this is also affected by the problems noted above. If directly determining the sample volume is difficult or inappropriate, an estimated material density can be used to calculate its volume from the measured weight [35].

Ideally, to calculate sample volume, the appropriate density to use is the average mass to volume ratio inside the surface defined by the volume inaccessible to H_2 in the absence of sorption. This may differ from the skeletal or theoretical crystal density of the unloaded sample and, in practice, can be quite difficult to define. The accessible volume of a microporous material, for example, depends on both pore geometry and the size of the probe [143,144]. Using an inaccurate sample density will obviously introduce an error in the calculated volume occupied by the sample. Analysis of such errors has shown that, for typical sample sizes and volumes in a manometric system, density errors of 25% can lead to uptake measurement errors greater than 100% over typical measurement pressure ranges [79]. This increases further with increasing pressure — see Fig. 4. The sample volume problem [81] is most acute for low density materials with highly porous or complex structures, which are often of interest in H_2 sorption studies.

Sample volume or density may also change during a measurement [145]. Alloys and intermetallics typically undergo crystal expansion during hydrogen absorption — $LaNi_5$, for example, expands by approximately 23% [40,146].
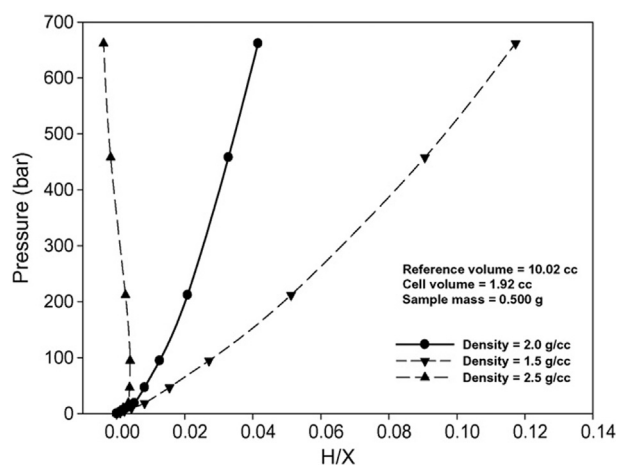
Fig. 4 — Effect of a ±25% change in sample density on the apparent hydrogen uptake of $C_{24}K$ at room temperature, measured in a system of insufficient volume relative to the volume of sample [79]. H/X is the hydrogen-to-host atomic ratio. (Reprinted from Journal of Alloys and Compounds, 446–447, T. P. Blach, E. M. Gray, Sieverts apparatus and methodology for accurate determination of hydrogen uptake by light-atom hosts, 692–697, Copyright (2007), with permission from Elsevier).

Similarly, Mg expands by approximately 30% during the transition from Mg to MgH_2 [39]. Complex hydrides, including borohydrides and alanates, also change density as the reaction proceeds, since a new compound is formed upon hydrogen absorption. Materials with layered structures, such as clays [147], may swell due to molecular H_2 penetrating layers. Structural phase transitions are also possible during adsorption by MOFs [148–150]. If it is known, the volume or density change as a function of pressure can be used to correct the calculated uptake. Otherwise, mitigation of the resulting effects is the only option.

Practically, two approaches can be used to help validate results when sample size is a concern. Firstly, if sample density is used to calculate uptake, the calculation can be repeated using likely lower and upper bound density values [98]. The variation in uptake for the extremes of density indicates the significance of any such errors, as shown, for example, in Fig. 4. Secondly, measurements can be made using different sample sizes. Any sample size dependence suggests problems with this issue as normalised hydrogen storage capacities (see Section Capacity definitions) are independent of the amount of sample used.

Figure of merit for the manometric technique

For manometric measurements, Blach and Gray [79] derived a figure of merit, η, to gauge the suitability of a system for a particular sample size. The sensitivity of a manometric instrument to changes in hydrogen content due to pressure changes during any sorption step is the slope of the isochore, s_k, which depends on sample size and the reference and sample cell volumes. To obtain η, s_k is divided by the pressure transducer resolution, δp. Blach and Gray [79] suggest that a minimum value of approximately 100 is required to obtain reliable results. Since η is proportional to sample size, it can be increased by using more sample. However, this increases the effects of uncertainty in the sample volume, as discussed above.

Figure of merit for the gravimetric technique

For accurate gravimetric results, the sample weight change as a result of sorption must be greater than the resolution of the microbalance and this will depend on sample size. We can define a simple expression, analogous to the Blach and Gray [79] figure of merit, for a gravimetric measurement, $\eta_g = M_H n_x / \delta m$, where M_H is the molar mass of hydrogen, n_x is the amount of sample in moles, as determined under vacuum at the start of the experiment, and δm is the microbalance resolution. The product $M_H n_x$ indicates the sensitivity to changes in the hydrogen content as measured by changes in the sample weight. Since η_g is effectively the ratio of sample weight to balance resolution, it can be increased by using more sample. However, larger samples lead to greater buoyancy effects so any uncertainty in sample volume contributes greater uncertainty to the calculated uptake. A compromise must again be found.

Degassed sample mass

Determining the degassed sample mass is a related issue, as any error in this will directly affect the calculated specific uptake for both techniques [35]. Although less problematic for hydrides, for nanoporous materials that lose a significant amount of weight during degassing due to removal of pre-adsorbed water or solvent, for example, the effects can be significant.

In the gravimetric case, weight is measured *in situ* so the degassed sample mass can, in principle, be determined accurately; however, the exact value must still be chosen [35]. For example, the sample mass at the end of the degassing process, at the degassing temperature, or the mass after the sample has reached the experimental temperature can be used. These should, in principle, be equal but some variation is often observed in practice.

In the manometric case, however, sample weight cannot be measured *in situ*. Therefore, appropriate steps must be taken, for example, by weighing the degassed sample in a glovebox or weighing the empty sealed sample cell under vacuum and the sealed cell containing the degassed sample under vacuum and subtracting one from the other. Sample cells can also be back-filled with an inert gas such as helium but, in this case, the empty cell must be filled with the same gas when weighed. Any of these methods could introduce errors. Regardless, using an erroneous sample mass is a measurement pitfall that can result in significant errors in the calculated H_2 uptake.

Sample and gas purity

Contamination of both the sample and the gas used for measurements must be carefully considered. Small quantities of an additive or impurity, intentional or otherwise, can have a significant impact on the interaction of H_2 with a material. Sample contamination can take a number of forms, each of which can create pitfalls when characterising the H_2 sorption behaviour of the material the sample is purported to represent. The considerations, in each case, depend on material type. Purity issues associated with sample preparation include contamination of the original constituents and contamination introduced during synthesis or during post-synthesis purification or treatment. Environmental contaminants can also be introduced by subsequently exposing synthesised samples to air. In this section, each of these issues is discussed, followed by consideration of gas purity.

Sample impurities

When samples are synthesised using commercial constituents, each component will have a nominal purity. Trace elements of similar atomic number that occur naturally together are often present, depending on the separation techniques or processing methods used. In many cases, the impurity type and approximate percentages can be obtained from the supplier [151]. However, other impurities, especially oxides and hydroxides for metals and metallic compounds, can be present [122,151], and these may also develop progressively on the surface of a material during storage and handling. Contamination of solid samples from container materials is likely to be less of a problem than for liquids [152,153]; however, it is worth noting that oxygen diffusion, for example, is possible through the walls of plastic containers – even those constructed from materials known to exhibit good barrier properties [154,155].

The synthesis process can also introduce impurities. For example, mechanical milling or ball-milling can result in contamination from the milling container and balls [156−160]. This is particularly relevant for hard materials, such as elemental hydrides, intermetallics and alloys, as well as other materials such as carbides [156,159,160]. When materials such as porous polymers [27,28,161−163] and borohydrides [164,165] are synthesised using wet chemistry methods, subsequent removal of solvent from the surface or pores is crucial. This must be performed thoroughly because residual solvent will likely interfere with subsequent H_2 sorption measurements. For MOFs, this is particularly important, and the process is known as *activation* [166,167]. Incomplete removal of solvent, or the activation method, has received considerable attention recently due to the important effect it can have on the properties of materials [166,168−170]. For example, activation using supercritical CO_2 has been found to significantly enhance the adsorption properties of some MOFs [167,169]. Separating the effects of this activation step from the degassing process prior to performing a H_2 sorption measurement is difficult but it is nevertheless important to ensure that MOFs are activated and degassed thoroughly. Ignoring this is a significant pitfall when characterising the H_2 adsorption properties of MOFs and related materials.

Successful activation and the purity of MOF samples can be assessed, to a certain extent, from pore structure and surface area analysis using, for example, N_2 or Ar adsorption at 77 K and 87 K, respectively [120]. Significant variation in the N_2 BET areas of different samples of the same MOF have been observed. De Lange et al. [114], for example, collated literature values for MIL-101(Cr). BET areas varied from approximately 1300 m^2 g^{-1} to 4200 m^2 g^{-1}, while pore volumes ranged from 1.1 cm^3 g^{-1} to 2.5 cm^3 g^{-1}. Large variations in reported H_2 uptakes for MOF-5, which correlate with BET area, were noted by Kaye et al. [171]. Differences for this material were attributed by Hafizovic et al. [172] to either the presence of Zn oxides in the pores or framework interpenetration, but related problems are likely for other MOFs.

Some materials must be purified following synthesis. A prominent example in hydrogen storage studies is purification or post-synthesis treatment of carbon nanotubes [173]. In one case, nanotube samples were sonicated using a Ti alloy horn, resulting in deposition of the alloy onto the material. It was later shown that absorption of hydrogen by the contaminant significantly affected the results [174,175].

For metal hydrides, sample purity problems can include compositional gradients in multicomponent alloys and the presence of minority phases in intermetallics [151]; though the presence of impurity elements in binary hydrides, which can result in formation of dilute substitutional alloys, may also alter their hydrogen sorption properties [7]. Compositional inhomogeneity in alloys and intermetallics can lead to changes in the shape of hydrogen sorption isotherms [151,176]. This can occur even in the absence of contaminants. Annealing alloys and intermetallics, using prolonged heat treatment in an inert atmosphere, can improve their compositional and structural homogeneity and reduce crystal imperfections, such as vacancies, dislocations and grain boundaries [60,151,177,178]. Crystalline minority phases present in large proportions can be detected using X-ray powder diffraction [151,179−181], for example, providing the amount is above the lower detection limit of this technique, which varies from material to material; but this technique alone should not be relied upon, due to the presence of phases that may go undetected. Large proportions of grain boundaries in ball-milled samples can also change the sorption properties of some hydrides [182] so this is another potential source of differences between samples. Thorough characterisation of the samples under study is therefore essential and ignoring potential effects of sample purity on any given result is another pitfall. Unfortunately, characterisation standards are not currently available for nanomaterials [183]. Developing such standards would be invaluable for addressing some of the points discussed above.

Environmental contaminants

Exposure to air can contaminate many materials. Light metals, for example, can oxidise rapidly, and relatively thick oxide layers can form on the surface of hydriding alloys after long term exposure [184−188]. Humidity is a problem for materials, such as hydrides, that may react with water. Nanocomposites including finely dispersed metals may be particularly susceptible to such contamination due to their large surface area to volume ratios. Most porous materials will also adsorb species from the atmosphere although the extent will depend partly on material type. For example, hydrophilic (low silica) zeolites can adsorb large quantities of water [116], but hydrophobic porous carbons will adsorb less, depending on the level of oxidation [116,189]. Other constituents of air, such as N_2, O_2 and CO_2, will also be present in micropores in varying quantities. These environmental contaminants must be removed prior to a H_2 sorption measurement. Some porous materials, including many MOFs, however, are also sensitive to moisture [190−192] and must therefore be handled in an inert atmosphere.

Ideally, degassing should be monitored to determine whether such environmental contaminants have been removed from the sample prior to a sorption measurement. However, despite the importance of this, degassing curves for nanoporous materials are rarely reported. Significant differences, for example, can be seen in the data presented by Tedds et al. [82] for a commercial carbon molecular sieve, a porous organic polymer (PIM-1), Na-X zeolite and two MOFs (MOF-5 and Cu-BTC). This issue is intrinsically linked to determination of the degassed sample mass (see Section Degassed sample mass). It also depends on the technique because sample weight can be measured accurately *in situ* using gravimetric apparatus but must be determined independently in the manometric case, as noted in Section Degassed sample mass.

Samples may also become contaminated through contact with the sample holder in an instrument. This can occur, in particular, when samples are heated. If chemical reactions take place during H_2 sorption, the sample holder may be in contact with highly reactive materials at elevated temperatures. A pitfall, in this case, is therefore use of a sample holder made from an inappropriate material.

Gas impurities

Another important consideration is the purity of both the H_2 gas used in the measurement and the helium used for

calibration [35]. Its significance depends on the types of impurity, the sample and the technique. Various impurities can be found in H_2 [193], any of which may preferentially adsorb, for example, to nanoporous adsorbents; or contaminate and poison the surface of metal hydrides [121,122,184], thus affecting the measurement. Some contaminants may also decompose sensitive samples such as complex hydrides. For nanoporous materials, it again depends partly on the sample properties. Any moisture in the supply, for example, will be readily adsorbed by a hydrophilic material but hydrophobic materials will be less susceptible. However, regardless of the hydrophobicity or otherwise of the sample, many gaseous contaminants will preferentially adsorb in comparison to H_2 due to the relatively weak physical interaction of H_2 with surfaces [194], in comparison to most other species. An obvious way of avoiding problems with contamination is simply to maximise the H_2 purity but it is important to note that contaminants can be present in gases supplied directly from a cylinder, regardless of the quoted purity. It has been found, for example, that additional moisture can be present in cylinders [71], most likely due to water condensation prior to filling with high purity H_2. Solutions are available, however, including purification systems [78] or specialised set-ups from commercial gas suppliers. Air Products, for example, provide BIP cylinders, which include filters that purify gas as it exits the cylinder (see, for example, Tedds et al. [82]). This type of high purity supply can be combined with special regulator configurations that minimise contamination during supply changes [35].

Use of such high purity supplies, however, may not be sufficient to ensure that pure H_2 is delivered to the sample because contaminants can be introduced in the gas supply path from the cylinder to the instrument. If long lengths of tubing are used to deliver H_2 from the cylinder, purification near to the instrument is one possibility. Molecular sieves — for example, zeolites and carbons — can remove moisture, hydrocarbons and other environmental contaminants, such as CO_2, from H_2 but an alternative is to use a liquid N_2 trap, which will freeze out any vapour phase species. Such traps have been used in a number of H_2 adsorption studies [75,82,163,195,196]. Another option is direct delivery of H_2 from a metal hydride bed, which can provide very high gas purities [55,98,184,185].

For some metal hydrides, contaminated H_2 can cause fewer problems, particularly when materials are relatively resistant to contamination, but this depends on material type. A classic example is $LaNi_5$ and its derivatives because these materials are thought to bind O_2 and H_2O on their surface in the form of La oxides or hydroxides, while metallic Ni clusters dissociate H_2 prior to absorption [121,184,185,197,198]; although some disagreement on the details exists [186] and large concentrations of O_2, for example, will still lead to degradation [185]. Other materials, most notably TiFe, however, are known to be more sensitive to impurities [36,37,184,199].

Regardless of differences between material types, however, using impure H_2 is a significant measurement pitfall. There have been well-documented incidences of moisture contamination leading to erroneous H_2 sorption results [71,72,74]. Contaminated H_2 should therefore be one of the first possibilities considered when anomalous H_2 sorption results are found, particularly for nanoporous materials and when using gravimetric methods due to the large mass signal of adsorbed impurity species compared to H_2. Gravimetric systems also tend to have larger internal volumes, thus providing a greater source of impurities [107]. Similarly, any impurities present in helium used to determine void volume in manometric instruments or the sample volume more generally may contaminate the sample and thus affect measurements.

Isotherm measurement procedure

Various aspects of the isotherm measurement procedure can adversely affect results. Insufficient consideration of the approach taken is therefore a significant pitfall, so the adopted strategy must be considered carefully. In this section, the choice of equilibrium dosing pressures or steps is considered. Equilibration times are discussed separately in Section Achievement of equilibrium.

General considerations

Isotherm measurement involves successive determination of H_2 uptake at progressively higher pressures at a constant temperature. For accurate results, it must be ensured that, at each point, the pressure at which the uptake is determined approximates the real equilibrium pressure. For nanoporous materials exhibiting fully reversible H_2 adsorption this may be less of an issue. However, for any material that absorbs hydrogen, in a closed system, true equilibrium is unlikely to be achieved because the pressure drive decreases to zero as the pressure approaches a constant value. Many metal hydrides exhibit strong exothermic absorption, together with hysteresis [35,200,201]. The experimental procedure thus becomes more important because pressure and temperature excursions are irreversible. At any step, when pressure is increased, the sample absorbs and the pressure then drops, following the isochore (constant volume) path to meet the isotherm at the uptake for the resultant pressure, as shown in Fig. 5.

For a sample exhibiting hysteresis, the pressure at this uptake value will not be the same if the approach differs, for
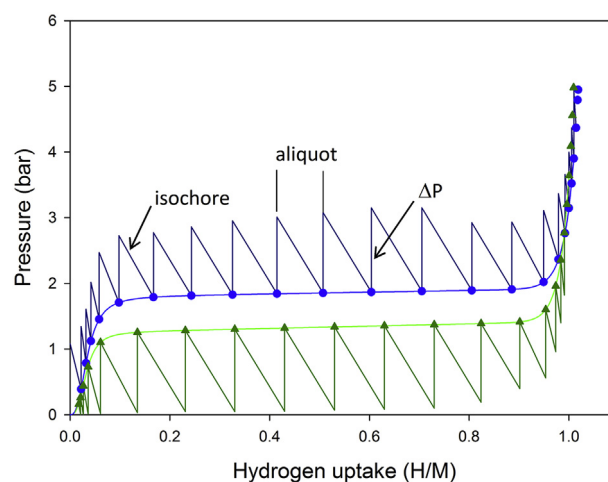
Fig. 5 – Absorption and desorption isotherms for $LaNi_5$ at 23 °C showing the pressure steps involved. H/M is the hydrogen-to-metal atom ratio.

example, if pressure is decreasing as for desorption. The same is true for temperature excursions. Since the equilibrium state depends on the pressure and temperature history of the sample, different values for the equilibrium pressure at a specific uptake can be achieved depending on the temperature path. As many metal hydrides of practical interest exhibit exothermic absorption and endothermic desorption, some of the approach to equilibrium in an increasing pressure step occurs at a different temperature until the sample cools to the nominal isotherm temperature, complicating both the pathway and thermodynamics. Ideally, small pressure steps induce only small pressure and temperature excursions [106], minimising the effect of intrinsic irreversibility. However, this increases the uncertainty in the calculated molar uptake in the manometric case, due to error accumulation, as described below. This is less of an issue when performing gravimetric measurements isobarically.

The large aliquot effect

A related complication for metal hydrides exhibiting hysteresis and a significant heat of reaction is the occurrence of the large aliquot effect [106,200,202–204]. If a large pressure step is applied to a homogenous sample, the entire sample begins to absorb strongly, generating heat due to the exothermic reaction. Parts of the sample far from the container wall or other heat sinks increase more in temperature than those close to heat sinks; absorption then slows or stops or it is possible these parts may even desorb. Material in close proximity to heat sinks, however, continues to absorb. This reduces the pressure, which, in turn, further increases the likelihood of desorption by higher temperature parts of the sample. This leads to compositional gradients in terms of hydrogen content – even after thermal equilibrium has been achieved [108,205]. As the sample cools, depending on the thermal conductivity of the bed, those parts of the sample that absorbed strongly may desorb and parts containing less hydrogen may begin to absorb. If desorption occurs at any stage, the resultant absorption isotherm will typically show a lower equilibrium pressure, closer to the desorption isotherm, depending on the chosen pressure step size [106].

To illustrate the compositional gradients that can occur in a metal hydride bed, Fig. 6 shows the calculated reacted fraction (proportion of hydride to non-hydride) for $LaNi_5$ subjected to a single aliquot of hydrogen. The measurements were made 5000 s after hydrogen loading, when thermal equilibration is complete. Material close to the actively cooled cell walls is almost fully hydrided, while material close to the cell centre is almost completely unreacted. The likelihood of such effects occurring in metal hydride beds during H_2 sorption measurement should not be ignored.

Isotherm points and propagation of uncertainties

More generally, the uncertainty in any sorption measurement depends on the uncertainty in all measured values, including temperature, pressure, volume and weight. These uncertainties propagate so careful consideration of the effects of this propagation is important. This is a particular concern for manometric measurements in which uncertainties accumulate through an isotherm [35,80,97]. Fig. 7 shows an adsorption isotherm with error bars from the calculated uncertainties
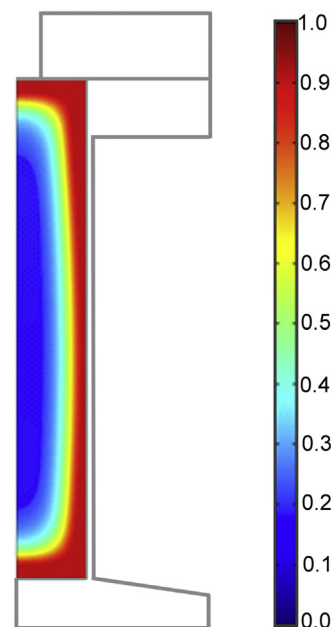

Fig. 6 – Calculated reacted fraction (proportion of hydride to non-hydride) for a $LaNi_5$ sample subjected to a single aliquot of hydrogen [205]. (Reprinted from International Journal of Hydrogen Energy, 42(10), S. S. Mohammadshahi et al., Experimental and theoretical study of compositional inhomogeneities in $LaNi_5D_x$ owing to temperature gradients and pressure hysteresis, investigated using spatially resolved in-situ neutron diffraction, 6793–6800, Copyright (2017), with permission from Elsevier).

demonstrating the accumulation of uncertainties with each successive pressure step. The main practical pitfall, in a well calibrated and validated system, is failure to consider this aspect of the measurement technique when setting the experimental parameters; principally the number of isotherm points [85]. A compromise must be found between the amount of information required, with regard to isotherm shape, and the accuracy of uptake determination. This is also important for gas adsorption measurements, in general [116].

Achievement of equilibrium

Isotherms describe equilibrium behaviour, so it is important to ensure that sorption is practically complete at each isotherm point [84]. An exception is when measurements are deliberately made under non-equilibrium conditions [96,203,206] but this is a special case not considered here. Rates of sorption or desorption vary significantly between material types, due to differences in the physical and chemical interaction of H_2 with different elements or compounds [7,36,37,122,194], but it also varies as a function of both temperature and pressure. Different approaches can be used to determine or define equilibration times but a simple mistake, for example, is to choose a fixed period that is too short for the process being investigated. The importance of this, for performing accurate equilibrium H_2 sorption measurements, cannot be overstated. This section considers this issue for different material types.
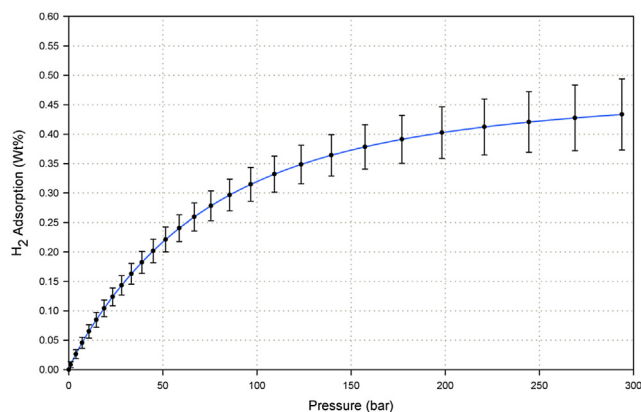
Fig. 7 – An adsorption isotherm for a commercial carbon molecular sieve, Takeda 4A, measured at 23 °C in a manometric apparatus, showing the error accumulation from successive doses [85]. (Reprinted from International Journal of Hydrogen Energy, 39(1), C. J. Webb and E. M. Gray, Analysis of the uncertainties in gas uptake measurements using the Sieverts method, 366–375, Copyright (2014), with permission from Elsevier).

Metal hydrides

The kinetics of hydrogen sorption by metal hydrides vary significantly between different host elements, alloys and intermetallics [7,122], but size effects are also important [207,208]. For intermetallics, intrinsic kinetics are often rapid and the approach to equilibrium is instead dominated by thermal equilibration following the increase in temperature from the exothermic reaction between H_2 and the material [104,105]. In other cases, absorption is slow and the approach to equilibrium is dominated by the intrinsic kinetics of hydrogen absorption or the rate of hydride phase formation. An example is Mg, which during absorption forms a (MgH_2) hydride shell on the surface in which hydrogen diffusion is slow [37,39,209]. Reaction kinetics and hydrogen diffusion rates vary significantly with temperature, typically following the Arrhenius relation at near-ambient temperatures and above [7,210,211], so this should also be considered. Kinetics can also vary significantly through the course of a single isotherm measurement. This has been demonstrated, for example, for Pd [100]. In the study by Benham and Ross [100], Pd foil was hydrided isobarically. At the start of the plateau, the absorption rate was found to drop dramatically due to the onset of β phase formation in the α phase matrix.

Functions can be fitted to uptake curves at each isotherm point, allowing use of numerical criteria to define achievement of equilibrium [100], which avoids the need to predefine fixed equilibration times. This minimises the length of an experiment because it can account for differences in sorption rates at different stages of the process, but it also helps avoid problems with insufficient equilibration by precisely defining the required conditions. A cruder approach is to simply wait for pressure or weight (and temperature) to stabilise in the manometric or gravimetric techniques, respectively. This is the main approach taken when making measurements manually.

Complex hydrides

Interaction between H_2 and elements or compounds that form complex hydrides differs fundamentally to absorption of atomic hydrogen, as screened protons, by metals forming interstitial metal hydrides. Complex hydride formation instead results from a chemical reaction between H_2 and the solid; and, in some cases, liquids [14]. This requires a phase transformation, resulting in formation of a compound containing, for example, hydrogen covalently bound in anionic metal complexes [9]. It is not within the scope of this article to discuss these aspects in detail – and, indeed, the mechanisms in many cases are not yet fully understood [10,14,212–214] – but the important point is to carefully consider the expected sorption process when defining experimental protocols. Hydrogen absorption by complex hydrides tends to be slow and it is even possible that the sorption kinetics of some materials are too sluggish for equilibrium to be achieved within a reasonable experimental timeframe. Extreme examples of this, with regard to hydrogen desorption, are kinetically stabilised materials such as AlH_3 [215–218] and $LiAlH_4$ [215,219].

Nanoporous materials

In contrast, H_2 adsorption by most nanoporous materials is rapid (see, for example, Panella and Hirscher [220] and Zhao et al. [221]). Adsorption kinetics are thus difficult to distinguish from thermal effects due to the adiabatic expansion of H_2 and the exothermic nature of H_2 adsorption. For materials that physically adsorb (or physisorb) H_2 at low temperature, no chemical reactions occur so the process is not complicated by the large amounts of heat generated during absorption of hydrogen by metal hydrides or by the rate of hydride phase formation. Thermal effects are always present but if they are insignificant the approach to equilibrium will instead be dominated by H_2 diffusion through the pore network or by entry of H_2 into the pores through the surface of each particle [222]. Nevertheless, for nanoporous materials, it is best to simply wait for pressure and temperature stabilisation in the manometric case, and weight and temperature stabilisation in the gravimetric case. A few minutes will often be sufficient [220,221], although this may depend on pressure [223].

Data reduction

Following a sorption experiment, measurements of temperature, pressure, and volume or weight need to be combined with the volume of the sample in order to calculate uptake. During this process, a number of assumptions must be made. Poor choices can lead to errors in the calculated quantity, regardless of the accuracy of the original measurements. Calculations must always be performed carefully but, in this section, we consider two important factors, namely, the description of the real gas behaviour of H_2, which is relevant to any H_2 sorption study performed at elevated (above ambient) pressure, and differences between the excess and absolute adsorbed quantities, which applies to H_2 adsorption by porous materials. In addition, different definitions of capacity are discussed.

Real gas behaviour

H_2 cannot be treated as an ideal gas, except under particular circumstances. For example, at ambient temperature and just

17 kPa, the relative difference between the non-ideal and ideal treatment of H_2 exceeds 0.01%, similar to the accuracy of a good pressure transducer. By 10 MPa, the difference is approximately 6%, while larger variations occur at lower temperatures – see, for example, Zhou and Zhou [224]. The compressibility factor, Z, must therefore be used in the majority of calculations. This can be determined using an equation of state (EOS). Many EOSs are available but accurate options are implemented in commercial packages, such as the NIST REFPROP database [225], which uses the Leachman et al. [226] EOS for H_2.

Different EOSs can generally be categorised as either cubic or multiparameter expressions. The former include the Soave-Redlich-Kwong [227] and Peng-Robinson [228] equations. These describe the pressure-density relationship in terms of the critical temperature, critical pressure and an acentric factor, which describes the non-sphericity of a molecule [229,230]. A hydrogen-specific EOS, based on the van der Waals EOS, was also presented by Hemmes et al. [231]. This was subsequently modified for D_2 by McLennan and Gray [232]. Multiparameter EOSs, meanwhile, include the Benedict-Webb-Rubin (BWR) equation [233] and its modified variants [234], and the Leachman et al. [226] expression. Further details can be found in Broom [35].

The effect of using different EOSs on the results of H_2 sorption measurements has been examined by a number of authors [76,224,235]. Significant differences in the calculated H_2 uptakes have been observed so the chosen EOS must be considered carefully.

Excess and absolute adsorption

An issue specific to H_2 adsorption by nanoporous materials [38,236] is consideration of excess and absolute adsorption. Treatment of adsorption in terms of excess quantities dates back to early work by Gibbs in the late 19th century [237]. It involves defining a reference state for adsorption by determining the position of the Gibbs dividing surface [116,120,142]. This can be assumed to represent the position of the surface of the solid, although this does not have to be the case – the key requirement is consistency. Nevertheless, helium is typically used under the assumption that it does not interact with the material under the measurement conditions [140–143]. This is intrinsically linked to consideration of the volume or density of the sample, as discussed in Section Sample size. However, for this discussion, it will be assumed that the initial position of the surface of the sample can be adequately determined using helium and that the same calculated sample volume is used for the duration of the experiment, regardless of changes in the sample. In this case, the calculated amount of adsorbed H_2 is the *excess adsorption*. This is defined as the amount of H_2 adsorbed over and above the H_2 that would be present in the same volume in the absence of any interaction between H_2 and the surface. Excess adsorption initially increases as a function of pressure, then reaches a maximum and decreases as the gas density increases further [38,143,235,236,238–243].

To estimate the total amount of adsorbed H_2, commonly known as the *absolute adsorption* [35,143,236,240,242,243], an additional calculation is required, based on an assumption about the adsorbed phase – the H_2 contained within the adsorption field of the material [236,244]. Two main

assumptions can be made. The adsorbed phase is considered to have either a constant volume or a constant density [236,244]. However, neither quantity is likely to be constant, nor can they be determined accurately by any known experimental technique, and assuming too large a volume or too low a density will lead to an overestimated absolute adsorbed quantity. Significant pitfalls when studying H_2 adsorption by porous materials are therefore insufficient consideration of differences between the excess and absolute and use of unrealistic assumptions to calculate absolute adsorption from the experimentally-determined excess. It should be noted, however, that the difference between excess and absolute only becomes significant at elevated pressures [236], as shown in Fig. 8, using the example of CH_4 adsorption on 13X (Na-X) zeolite.[3]

An alternative definition is *net adsorption*, as proposed by Gumma and Talu [137]. This circumvents problems associated with defining or determining the sample volume and is defined as the amount of H_2 adsorbed over and above the H_2 that would be present in the same volume in the absence of any sample. For H_2 storage, this definition is useful for determining the performance of a tank filled with adsorbent compared to one containing only compressed H_2 and in identifying the pressure at which a maximum in the storage capacity is reached, in comparison to gas compression alone [243]. Net adsorption is yet to be widely adopted but further investigation of its use in adsorption studies may lead to its wider acceptance.

Capacity definitions

In addition to considering excess and absolute adsorption, hydrogen uptake capacity is reported in various ways that can depend on the application. For H_2 storage, the ratio of the weight of H_2 to the system weight (kg H_2/kg) is an effective gravimetric measure, whereas the amount of H_2 per unit volume of the system (kg H_2/l) gives a volumetric capacity. System weight or volume can include the material, tank and accessories, such as heat management and safety devices. Gravimetric and volumetric system capacities can also be expressed in terms of the energy available in the H_2 as kWh/kg and kWh/l, respectively [246].

When focussing only on the material, volumetric capacity can be defined as the quantity of hydrogen per unit volume, for example, the crystal cell volume for hydrides [36]. Alternatively, the number of absorbed hydrogen atoms can be expressed as a stoichiometry, for example, x in $LaNi_5H_x$, or as a hydrogen-to-metal atom ratio (H/M), so that, for example, H/M = 1 for $LaNi_5H_6$; these approaches ignore volumetric or gravimetric considerations so they are less useful for storage applications but are favourable for fundamental work. For example, it is more helpful in crystallographic studies to consider the number of H atoms present in each unit cell, as compared to volumetric or gravimetric capacities. For adsorbents, a common unit is mol g^{-1} [120]. This is effectively a gravimetric capacity, expressed as a ratio of the molar

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[3] CH_4 adsorption data was chosen for Fig. 8 because it more clearly illustrates the difference between excess and absolute, and the peculiar behaviour of the excess, than any published H_2 adsorption data of which the authors are currently aware.
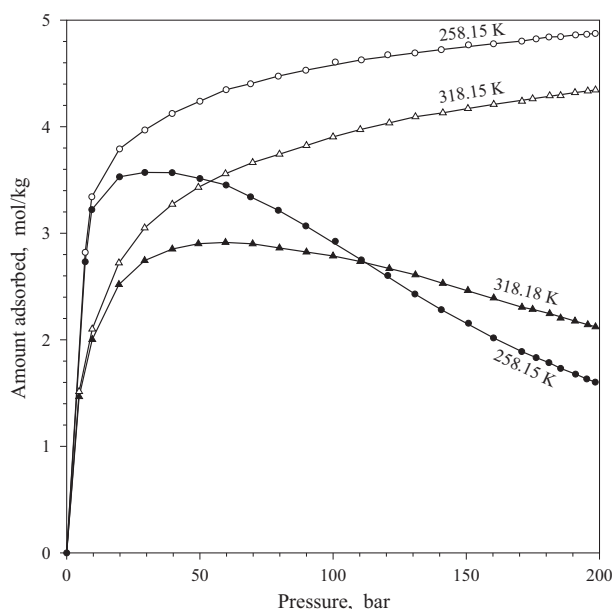
Fig. 8 – Absolute and excess isotherms for adsorption of CH₄ on 13X molecular sieve at 258.15 K and 318.15 K. Closed symbols: experimental data for excess adsorption [245]. Open symbols: absolute adsorption [243]. (Reproduced from Adsorption, Physical adsorption of gases: the case for absolute adsorption as the basis for thermodynamic analysis, 20, 2014, 591–622, A. L. Myers, P. A. Monson. Copyright Springer Science + Business Media New York 2014. With permission of Springer).

quantity of adsorbate (H_2) to the dry weight of the sample. However, for both hydrides and adsorbents, material capacity is commonly quoted in wt% – a percentage ratio of the weight of hydrogen stored to the weight of the material. To further complicate matters, there are two ways to calculate wt%, either from the ratio of hydrogen weight to the weight of the material alone [35,188], or the ratio of hydrogen weight to the weight of the material including hydrogen [35,36]. As an example, for $LaNi_5H_6$, the former method gives a gravimetric capacity of 1.40 wt% and the latter, 1.38 wt%. For $Mg(BH_4)_2$, the differently calculated capacities are 17.6 wt% and 14.9 wt%, respectively. The relative importance of using the different definitions therefore differs between material types.

Capacity can therefore be expressed in a variety of ways and it is important that consistent methods are used when making comparisons. Furthermore, some materials do not completely desorb, or they only desorb fully at impractically high temperatures for some applications. The latter is a particular issue, for example, for hydrogen storage in complex hydrides [14,37]. The capacity of a material in the practical part of the sorption-desorption cycle can be referred to as the *reversible* or *usable capacity*, as compared to the total capacity [36]. In addition, intended applications typically impose restrictions on pressure and temperature that limit the range over which the material can practically sorb and desorb H_2, even if complete desorption is possible. For example, for automotive H_2 storage, delivery pressure is the minimum feed pressure for a fuel cell [247], and the storage temperature

should be within safe limits and not incur significant energy penalties. Some materials may have a high total capacity but sorption involves multiple processes, some of which are not kinetically or thermodynamically viable, restricting the amount of H_2 that can be reversibly sorbed. In this case, for a particular application, the usable or reversible capacity can be defined as the amount of H_2 that sorbs and desorbs between the upper and lower pressures, within a practical timeframe and the required temperature range [36,82,242,248].

From a technological perspective, usable capacity is most important, but for fundamental studies the total hydrogen content may be more meaningful. Calculating the capacity of a material inappropriately can therefore be considered another pitfall in the characterisation of the hydrogen sorption properties of materials.

Discussion

In this article, we have identified and described potential pitfalls in the characterisation of the hydrogen sorption properties of materials. If these are avoided, in principle, accurate measurements can be made. However, difficulties relating to the nature of the material being investigated and the suitability of a given apparatus to the sample and measurement type become more significant as measurements become more challenging so, in some cases, particular care is required. A notable example from the literature is the study by Liu et al. [249] who revisited earlier work on carbon nanotubes. In their 2010 study, the authors acknowledged that the apparatus they used previously [92] was not sufficiently accurate for carbon nanotubes because, while it was designed to make accurate measurements on high density metal hydrides, system errors due to pressure accuracy, temperature fluctuations and sample volume determination were all amplified by using a low density sample in a small sample cell.

The disparity in the data found in the recent interlaboratory exercises, which demonstrated poor reproducibility between international laboratories, is certainly a cause for concern. The H_2 adsorption measurements reported by Zlotea et al. [94] are particularly prone to error for a number of reasons. Firstly, low temperatures (77 K) and pressures up to 10 MPa are conditions under which these measurements are more difficult, resulting in lower accuracy. Secondly, H_2 adsorption measurements made at ambient temperature are challenging because uptakes are lower under these conditions, due to the weak van der Waals interactions of H_2 with surfaces. The equivalent absolute uncertainty in each measurement thus represents a large proportional uncertainty, leading to a greater expected percentage variation in the results, regardless of any systematic errors. Thirdly, errors are greater for low density materials [79], of which porous carbon is a good example.

Variations seen in the data for the MgH_2-based material [95] are maybe more surprising, for the following reasons. Firstly, hydrogen absorption by hydrides is generally more straightforward than H_2 adsorption by nanoporous materials because issues related to excess and absolute adsorption (Section Excess and absolute adsorption) do not apply; though changes in sample density during absorption (Section General

considerations) can be considered analogous. Secondly, MgH_2 and modified variants have been widely studied — hundreds of results can be found in the literature. Pure MgH_2 is also known to have a maximum theoretical hydrogen storage capacity of 7.6 wt%. In contrast, for example, the uptake for carbon-based materials is unknown and a maximum theoretical capacity cannot be determined, so results have been reported without censure, giving rise to some high profile controversies [88]. Thirdly, all groups involved in the study by Moretto et al. [95] have experience of measuring hydrogen sorption so awareness of the pitfalls described above could be expected.

Pinpointing the reasons for the discrepancies is difficult; however, the Mg-H_2 reaction presents experimental challenges that could exacerbate some of the problems. The enthalpy of formation, for example, is high, at -75 kJ mol^{-1} [39,250], leading to significant temperature changes during absorption and desorption. The kinetics are also slow and highly temperature dependent. Judging equilibrium is more difficult for slow reactions and long equilibration times place additional requirements on thermal stability and leak integrity. Failing to wait for equilibrium can introduce experimental artefacts such as shortened equilibrium plateaux, hysteresis and inaccurate thermodynamic properties [251]. These factors may therefore help explain the observed disparity.

Regardless, if an attempt by Moretto et al. [95] to obtain agreement between different laboratories using apparently identical samples led to such variations in the measured uptake, this leads to the rather obvious question regarding the veracity of individual reports in the literature of the hydrogen sorption properties of different hydrides. So this is not just an issue for H_2 adsorption by nanostructured carbons and related materials, which have been the main focus of recent controversies [88]. It also emphasises the need to increase our understanding and appreciation of the pitfalls involved in H_2 uptake measurements and how to avoid them. One way of identifying specific problems with irreproducibility would be to perform further interlaboratory exercises, accompanied by thorough investigation of precise differences between the apparatus and measurement protocols of the participants. However, such studies would require a considerable amount of time and effort, and hence funding.

It is worth emphasising that a number of approaches can be used by individual researchers to increase confidence in the veracity of results. Prior to commencing experimental work, for example, the equipment, calibrations and data processing methods can be checked by routine measurement of empty cell or sample holder isotherms and H_2 sorption isotherms on well-understood materials (Section System validation). Measurements can be validated by repeating the experiment under differing conditions to verify repeatability and to investigate the effects of using different sample sizes, varying the number of isotherm points and varying equilibration times. Consistency of the isotherm calculations can be checked by repeating calculations with a range of sample density values (Section General considerations) and by changing the equation of state (Section Real gas behaviour). Significant discrepancies observed in calculated equilibrium H_2 uptake values can provide clues to areas of particular sensitivity for both the apparatus and sample, and help

researchers identify when measurement error may be important. A particularly useful approach is to use different techniques, for example, both gravimetric and manometric measurements. Use of such cross-checks should therefore be encouraged to help avoid the pitfalls described in this article. A simple validation for any result is to repeat the experiment, preferably three or four times or more [252] — as Hibbert and Thordarson [252] say: "*It is dangerous to report results based on a single experiment.*" While not guaranteeing reproducibility between different laboratories, repeatable results provide confidence that spurious errors or random variations have been avoided.

Before concluding, it is also worth noting that some of the practical difficulties of H_2 adsorption measurement are shared by measurements of the adsorption of other gases. A number of studies, for example, have discussed the issues for the measurement of CH_4 and CO_2 adsorption by porous materials [253–257]. Interlaboratory exercises have also been performed on activated carbons [258] and natural materials such as coals [259,260] and shales [261]. Common ground exists between these measurement types. The most significant difference between them is the differing physical properties of the gases, which are generally accounted for by using different equations of state, but other factors complicate a direct comparison. For example, for gravimetric measurements, H_2 sorption is more challenging to measure due to its low molar mass. However, CO_2 adsorption can be difficult to measure under certain conditions due to the strong dependence of its compressibility factor on temperature and pressure near its critical point [253,256,257]. Nevertheless, many of the pitfalls identified in this article also apply to CO_2 and CH_4 adsorption measurements, as discussed in some detail by Gasparik et al. [261]. Related work in other fields can also be found in the literature, including gas sorption by polymers [112], N_2 adsorption for surface area determination [135,262–264] and high pressure gas adsorption, more generally [265–268]. Progress made in any of the above fields may therefore benefit the others.

Conclusions

This article has discussed potential pitfalls encountered in the measurement of hydrogen sorption by different materials. They have been grouped into issues associated with instrument design and calibration, sample size, sample and gas purity, isotherm measurement procedure, achievement of equilibrium, and data reduction. While a basic manometric sorption measurement system is not difficult to construct from off-the-shelf components, any of the pitfalls addressed in this article can significantly affect the obtained results. Commercial instruments capable of making H_2 sorption measurements are available from various suppliers. However, the error sources inherent to both manometric and gravimetric sorption measurements mean that even high accuracy commercial units should not be treated as "black boxes" and therefore all considerations covered in this article should be taken into account when defining experimental protocols, performing experiments, analysing data, and assessing likely errors and uncertainties. Hopefully, as awareness of the problems that can occur when characterising the H_2 sorption

properties of materials continues to grow, the quality of published data will also improve. We hope this article will contribute positively to such improvements.

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