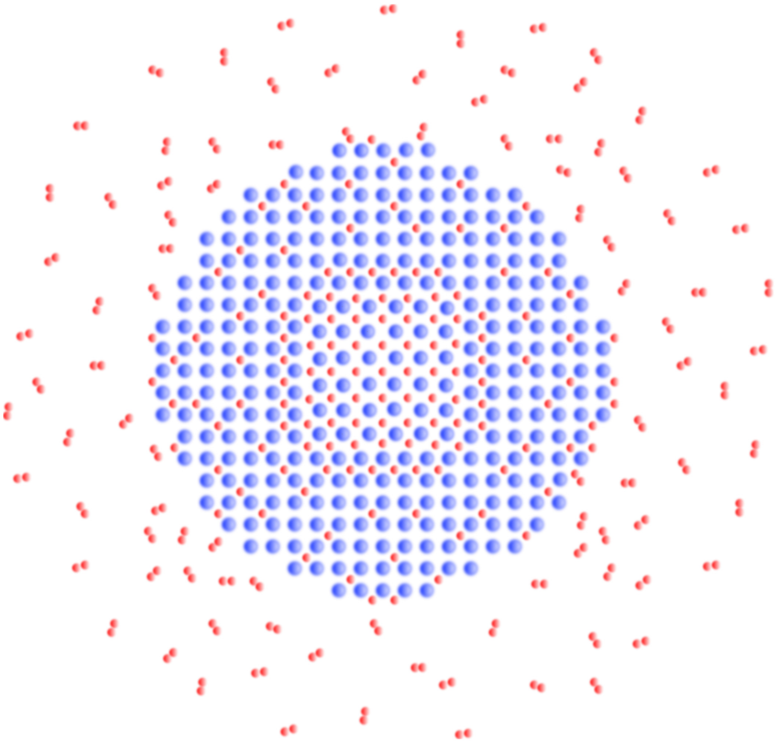
JRC Scientific and Technical Reports

HYDROGEN SORPTION MEASUREMENTS ON POTENTIAL STORAGE MATERIALS

Experimental Methods and Measurement Accuracy

D. P. Broom



EUR 23242 EN - 2008

EUROPEAN COMMISSION

Institute for Energy

The Institute for Energy provides scientific and technical support for the conception, development, implementation and monitoring of community policies related to energy. Special emphasis is given to the security of energy supply and to sustainable and safe energy production.

European Commission
Joint Research Centre
Institute for Energy

Contact information
Address: Post Office Box 2, NL-1755 ZG Petten
E-mail: pietro.moretto@jrc.nl
Tel.: +31 (0)224 565656
Fax: +31 (0)224 565600

http://ie.jrc.ec.europa.eu
http://www.jrc.ec.europa.eu

JRC 43223

EUR 23242 EN
ISBN 978-92-79-08345-7
ISSN 1018-5593
DOI: 10.2790/86100

Luxembourg: Office for Official Publications of the European Communities

Printed in The Netherlands

ABSTRACT

The hydrogen storage problem is one of the major issues that needs to be resolved if hydrogen is to become a viable energy carrier in the future. An earlier EUR report [1] examined the problem, including its possible solution through the use of a solid state storage material. This option is one of the most attractive for a number of reasons, although no material currently satisfies the practical requirements, in terms of storage capacity, operating temperature and pressure ranges, impurity resistance, long term cycling stability and cost. The search for a material that fulfils the criteria for a practical store is therefore generating a great deal of scientific research interest, and an increasing number of publications on this topic are appearing in the scientific literature.

A crucial part of the search for new storage materials is the accurate determination of the hydrogen sorption or storage characteristics of new or modified materials. This is an issue that has come to prominence in recent years due to the controversy over the potential storage capacity of carbon nanostructures, such as nanotubes and nanofibres, during which widely varying claims of potential storage capacity and hydrogen uptake behaviour were made. A significant contribution to this controversy was made by inaccuracy in the measurement of the potential gas phase hydrogen storage capacities of these nanostructured carbon materials.

This report focuses on the gas phase, as opposed to electrochemical, characterisation of the equilibrium hydrogen sorption properties of potential storage materials, and covers the common techniques that can be used to determine the hydrogen uptake behaviour of potential hydrogen storage media. The latter part of the report concentrates on the accuracy of these measurement techniques and discusses the possible sources of error in these methods with reference to previous work that has appeared in the scientific press, as well as existing measurement standards and guidelines. In addition, checklists of the issues that affect the accuracy of hydrogen sorption measurement, in the case of absorbers and adsorbents, based on the discussion presented here, are tentatively proposed. The Appendix also includes a discussion of the conversion of the experimentally-determined hydrogen adsorption parameter, the excess adsorption, to a total, or absolute, adsorbed quantity. The part of this report that addresses measurement accuracy is based on a review article published recently in the International Journal of Hydrogen Energy [2].

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BS EN	British Standard European Norm
BWR	Benedict-Webb-Rubin (EOS)
DOE	US Department of Energy
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EGA	Evolved Gas Analysis
EOS	Equation of State
GCMC	Grand Canonical Monte Carlo
IUPAC	International Union of Pure and Applied Chemistry
JIS	Japanese Industrial Standard
MFC	Mass Flow Controller
MH	Metal Hydride
MOF	Metal Organic Framework
MS	Mass Spectrometry
Ni-MH	Nickel-Metal Hydride (batteries)
NIST	National Institute of Standards and Technology
PCI	Pressure-Composition Isotherm
PCT	Pressure-Composition-Temperature
PSD	Pore Size Distribution
SRK	Soave-Redlich-Kwong (EOS)
SRM	Standard Reference Material
SSA	Specific Surface Area
STP	Standard Temperature and Pressure
TDS	Thermal Desorption Spectroscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TGA-MS	Thermogravimetric Analysis-Mass Spectrometry
TPD	Temperature Programmed Desorption
UHV	Ultra High Vacuum
VDW	van der Waals (EOS)

GLOSSARY OF SYMBOLS

A	A set of adsorbate molecules
$A_{orifice}$	Cross-sectional area of a leak source
B	Empirical coefficient of the Antoine Equation
c_p	Specific heat capacity of a gas at constant pressure
c_v	Specific heat capacity of a gas at constant volume
C	Empirical coefficient of the Antoine Equation
C_f	Final hydrogen concentration (H/M)
C_i	Initial hydrogen concentration (H/M)
$C_{wt.\%}$	Gravimetric hydrogen storage capacity
d	Tube diameter
D	Empirical coefficient of the Antoine Equation
DC	Discharge coefficient
f	Fugacity
H/M	Hydrogen-to-metal atom ratio
Kn	Knudsen number
K_α	An absorption coefficient for a given hydriding alloy
L	Characteristic length scale of a system
m	Sample mass
m_a	Measured adsorbed mass, the Gibbs excess mass
m_{ref}	Mass of a non-adsorbing reference fluid
m_{system}	Total mass of fluid (gas) in the adsorption system
m_{tot}	Total adsorbed mass, the total or absolute adsorption
$\dot{m}$	Mass flow rate
M	Molecular weight / Molar mass
M_H	Molar mass of hydrogen
M_{Host}	Molar mass of host material
n_a	Measured adsorption, the Gibbs excess in moles
Δn	Number of moles ad- or absorbed
N_a	Number of atoms per formula unit
δp	Useable resolution of a pressure measuring device
P	Pressure

P_0	Empirical characteristic pressure for a given tube diameter
P_c	Critical pressure of an adsorbate
P_f	Final pressure
P_i	Initial pressure
P_m	Measured pressure
P_s	Pseudo saturation vapour pressure of a supercritical adsorbate
P_t	True pressure
P^0	Saturation pressure of an adsorbate
R	Universal gas constant (8.314 J K^{-1} mol^{-1})
R_m	R/M, for a given gas
s_k	Sensitivity of volumetric apparatus to changes in sorbed hydrogen
S	Specific surface area of an adsorbent
T	Temperature
T_b	Boiling temperature
T_c	Critical temperature of an adsorbate
T_m	Measured temperature
T_t	True temperature
v_g	Molar volume of adsorbate
V	Volume
V_a	Volume of adsorbate layer, $V(A)$
V_f	Bulk fluid (gas) phase volume
V_m	Measured temperature
V_s	Sample volume
V_{solid}	Volume of adsorbent in an adsorption system of volume, V_{total}
V_{sys}	System volume
V_{total}	Total volume of adsorption system
V_1	Calibrated dosing volume (in volumetric apparatus)
V_2	Sample cell volume (in volumetric apparatus)
w	Apparent sample weight after sorption
w_0	Sample weight in vacuum
Δw	Apparent sample weight change upon sorption
x_a	Thickness of adsorbed phase layer
$Z_{P,T}$	Hydrogen compressibility factor, at pressure P and temperature T
α	Thermal expansion coefficient of a superheated liquid

γ	Ratio of the specific heat capacities of a gas at constant pressure
η	Figure of merit design parameter for volumetric apparatus
λ	Mean free path of a hydrogen molecule
ρ	Sample density
ρ_a	Adsorbate phase density
ρ_c	Critical density of an adsorbate
ρ_H	Bulk gas phase hydrogen density
ρ_{liq}	Liquid density of an adsorbate
$\rho(\boldsymbol{x})$	Adsorbate density at a point $\boldsymbol{x}$
σ	Molecular diameter of an adsorbate molecule
χ	Exponent in thermal transpiration pressure measurement correction

LIST OF FIGURES

1 INTRODUCTION

The search for potential hydrogen storage materials has recently been receiving a great deal of attention, as the hydrogen storage problem is one of the major issues that needs to be resolved if hydrogen is to become a viable energy carrier in the future [3]. The search for new materials and the various proposed solutions to the problem have both been covered in a number of recent review articles [3-11]. Aside from the so-called 'chemical hydrides' [12], the materials currently being considered can be broadly separated into two categories: one in which the hydrogen is absorbed in the bulk of the material in atomic form and the second in which the hydrogen is weakly bonded in molecular form to the surface of the material. The former is hydrogen *ab*sorption and the latter hydrogen *ad*sorption[1]. Both of these processes can be measured or monitored using bulk gas phase characterisation methods that loosely mimic the process by which a practical solid state hydrogen store would be charged or discharged. Volumetric and gravimetric techniques determine the hydrogen sorption properties of a material by exposing it to a pressure of hydrogen at a given temperature, causing a reaction that results either in the sorption or desorption of hydrogen, depending on whether there has been an increase or decrease in the applied pressure from the previous step. The measured hydrogen content at different hydrogen pressures is then plotted to form an isotherm. Temperature-programmed techniques, on the other hand, use temperature changes to sorb and desorb the hydrogen. An experiment therefore consists of taking the sample from a low temperature, at which hydrogen is thermodynamically or kinetically trapped in the material, to a higher temperature, at which the hydrogen will be partially or fully desorbed, and monitoring the quantity of hydrogen released.

These types of sorption measurements have previously been performed for a number of different reasons. In metal hydride research, the measurement of the absorption of hydrogen by elemental metals and intermetallic compounds has been made for reasons ranging from understanding the fundamental interaction of hydrogen with matter [14-19] to the development of specific technological applications, both gas phase [20], such as metal hydride heat pumps, and electrochemical, such as nickel-metal hydride batteries [21-23]. The measurement of gas adsorption on porous materials, meanwhile, is another mature research field in which measurements have been made using similar techniques to those of hydride research but for the purpose of surface area, pore size distribution (PSD) and porosity determination. However, for a number of reasons, hydrogen is not a common probe gas[2], and so there is a great deal more literature available on the adsorption of the typical probe gases compared to the adsorption of hydrogen [26]. Although there are many similarities between the methods used for these measurements, there are also issues that are specific to hydrogen sorption and, in particular, to the application of gaseous hydrogen storage.

---

[1] The term *sorption* will be used in this report to encompass both meanings and their variants (molecular physisorption, atomic chemisorption, atomic absorption, and so on) [13].

[2] Unlike, for example, nitrogen, argon and carbon dioxide [24]; although in catalysis hydrogen chemisorption is used for the determination of active metal site areas [25].

1.1 Adsorption Measurement

Typical (non-hydrogen) adsorption measurements are performed at sub- or near-critical temperatures, with the isotherm expressed in terms of relative pressure, P/P^0, where P^0 is the saturation pressure of the adsorptive (atmospheric pressure in the case of nitrogen at 77 K). An example being routine BET specific surface area (SSA) measurement. There are IUPAC isotherm classifications (types I to VI) [27], that are commonly used to assess adsorption isotherms, but these apply only to condensable vapours [28] and therefore do not apply to hydrogen at the temperatures of practical interest for storage applications (generally 77 K or above). For reasons of practicality, the adsorption behaviour of hydrogen at or below its critical temperature (33 K) is not of great interest[3] for storage applications [29,30], and we are therefore interested in the measurement of *supercritical adsorption*[4]. Furthermore, for storage purposes, the gaseous hydrogen will need to be stored and released at above ambient pressures; therefore, generally speaking, we are interested in higher absolute pressure measurements than those routinely performed for surface area, PSD and porosity determination using other gases[5]. Good, although brief, overviews of gas adsorption instrumentation, along with information on commercial suppliers, have been given by Keller and co-workers [24,41]. The monographs by Rouquerol et al [26] and Keller and Staudt [40] cover gas adsorption measurement apparatus in far greater detail.

1.2 Absorption Measurement

In contrast to adsorption measurements, which are often performed at lower (sub-ambient) temperatures, absorption measurements on hydrides are typically determined at higher temperatures, as well as above ambient pressures. Isotherms for the AB_5 intermetallic hydrides, and many other hydrogen-absorbing alloys [4], for example, can be measured from below ambient temperatures upwards [42], with many of the new complex and nanocrystalline hydrides currently being investigated requiring elevated temperatures of over 300 °C [43]. Different hydride operating temperature ranges are defined in a Japanese Industrial Standard (JIS H 7003) [44] in terms of the standard decomposition temperature, which is defined as the temperature at which the dissociation[6] plateau pressure [4] becomes 1 atmosphere (101.3 kPa). *Low temperature* hydrides, according to the JIS definitions, have a standard decomposition temperature below 50 °C, *medium temperature* hydrides between 50 and 200 °C and *high temperature* above 200 °C. The plateau pressure is an important parameter in the characterisation of hydrides [4] and, unless the hydride is particularly stable,

---

[3] Hydrogen adsorption is also studied at subcritical temperatures but this tends to be for more fundamental studies [31-35].

[4] *Supercritical adsorption* is the term used for adsorption measurement or the adsorption process above an adsorptive's critical temperature. The excess adsorption at supercritical temperatures will tend to reach a maximum at elevated pressures before then decreasing [28,30,36-38]; this occurs at pressures significantly higher than ambient (see Appendix A and Figure 6).

[5] There are, of course, numerous exceptions [39], and supercritical adsorption is crucial in other application areas, such as gas separation. See the Introduction and the first chapter of Keller and Staudt [40] for an overview of the range of different practical applications.

[6] Although the hydrogen dissociation process is associated with hydride formation rather than decomposition.

performing measurements only below ambient pressure will greatly limit the amount of information that can be obtained[7].

1.3 Report Structure

In this report, the techniques that are readily available for the performance of gas phase sorption measurements, for the specific purpose of the quantification of gaseous hydrogen uptake and release, are described. Examples are given of experimental systems that have been reported in the literature. References to the use of each technique for the characterisation of a range of storage materials, including both absorbers and adsorbents, are also given, and some practical considerations for the choice of instrumentation are discussed. The latter part of the report focuses on the issues surrounding the accuracy of hydrogen sorption measurements.

More specifically, Sections 2 to 4 cover the volumetric, gravimetric and temperature-programmed techniques, respectively, while Section 5 discusses some of the practical aspects of the choice of instrumentation. Section 6 then introduces the topic of hydrogen sorption measurement accuracy and reviews published work in the area. A number of sources of experimental error are then described and discussed in Section 7, with a conclusion given in Section 8. Finally, in the Appendix, an issue related to adsorption measurement accuracy, the definition of the total adsorbed quantity, is discussed, and a summary of the experimental error sources for volumetric and gravimetric sorption measurement is presented in the form of four tentative measurement checklists.

---

[7] For example, a routine van ’t Hoff plot, the log of plateau pressure vs inverse temperature, typically requires five data points; therefore, isotherms would be required at five temperatures with all having plateaus below ambient pressure. For hydrides in the useful temperature and pressure region for storage purposes, this is unlikely.

2 VOLUMETRIC TECHNIQUES

2.1 Description

The *volumetric* technique determines the amount of hydrogen ad- or absorbed by a sample by monitoring the drop in hydrogen pressure in a fixed volume in direct contact with the sample. During the desorption process, the quantity of hydrogen released is determined by the increase in the hydrogen pressure, following evacuation of some or all of the hydrogen in the gas phase. To illustrate the principle, Figure 1 shows a schematic diagram of a basic volumetric set-up. V1 and V2 are known volumes, of volume V_1 and V_2, and valves A and B control the hydrogen gas inlet and vacuum outlet, respectively, allowing the control of the hydrogen pressure in V1. Valve C allows the introduction or removal of gas to or from V2, and the pressure in V1 is measured using the manometer. The sample sits at the bottom of V2, with a temperature sensor (not indicated in the diagram) either near or in contact with it. As with all of the measurements described in this report, the sample should be secured appropriately, although this will depend on the form of the sample (for example, a fine or coarse powder, foil, single crystal, and so on). The thermostat or thermal bath can be any temperature-controlling system, including a liquid N_2 dewar, a cryostat, a low temperature fluid bath or a furnace. The temperature of the system should be controlled and monitored, with temperature sensors in more than one position, preferably including the measurement of the gas temperature away from the sample. The manometer represents one or more pressure measuring devices, depending on the hydrogen pressure ranges required. In a system designed for both low and high pressures, this is likely to include separate gauges for different ranges. The generic vacuum pump can be of any type, although an oil-free system with a ultra-high vacuum (UHV) compatible pump (for example, turbomolecular) would be preferable, particularly if samples are to be degassed (in the case of porous adsorbents) or if measurements are to be made at low pressures ($< 10^2$ Pa, for example). An oil-free system is favourable because oil vapour can backstream into the system causing contamination[8]; although oil vapour filters can reduce this, they are unlikely to eliminate it entirely. The hydrogen supply should be of very high purity (> 99.999 %) and/or filtered adequately.

2.1.1 Hydrogen Absorption

To perform a simple, single step absorption experiment on an activated[9] sample in the apparatus shown in Figure 1, valves B and C are first opened to evacuate V1 and V2. After sufficient time, valves B and C are then closed. Valve A is opened, allowing V1

---

[8] A study by Bojon et al [45] showed that a turbomolecular pumping station, backed by a rotary oil pump, did not significantly contaminate a UHV system during operation, but water and hydrocarbon contamination was introduced upon stoppage of the pump. Volumetric systems designed for hydrides can operate without UHV-capable pumps; in this case, it is very important that the vacuum pump does not introduce contamination and therefore an oil-free device, such as a scroll pump, should be used.

[9] Prepared for hydrogen sorption. *Activation*, with regard to hydrogen-absorbing alloys, is defined in JIS H 7003 [44] as “a pretreatment for promotion of reaction for absorption and desorption of hydrogen of an alloy”, although it can take many forms [13].

to fill with hydrogen to an initial pressure P_i. Valve C is then opened thus filling V2. Any drop in pressure beyond that which is expected from the volume difference between V_1 and $(V_1 + V_2)$ is then assumed to have resulted from the absorption of hydrogen. So, assuming the experiment is performed at a constant temperature, T, and that the final measured pressure is P_f, the number of moles sorbed is given by,

$$\Delta n = \frac{P_i V_1}{RT} - \frac{P_f (V_1 + V_2)}{RT} \tag{1}$$

where R is the universal gas constant.

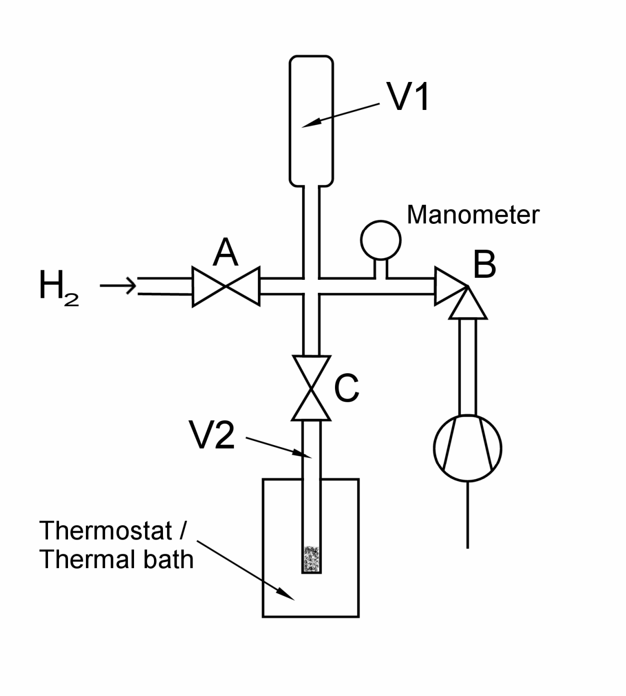


Figure 1. A schematic diagram of volumetric sorption apparatus.

To extend this measurement to a full isotherm, the subsequent step would then use the values of Δn and P_f as a starting point. The repetition of the above procedure will result in the measurement of a complete absorption isotherm. This description of the principle ignores both the compressibility of the gas and the expansion of the hydride (and subsequent reduction in the dead space volume) during the absorption process, and any consideration of temperature difference between the system and the sample. The compressibility, $Z_{P,T}$, appears in both the terms on the right hand side of Eq. (1). In each case the value of Z corresponds to the particular pressure, P, and temperature, T, of the hydrogen at the time of the measurement. The difference in temperature can be accounted for by assuming that there is a fixed dividing line between the two temperature regions. Although this will not practically be the case, the effective dividing line for a particular sample cell temperature can be determined during calibration measurement.

2.1.2 Hydrogen Adsorption

An adsorption experiment follows the same principle, although in this case the quantity determined by the drop in pressure is the *excess adsorption* (see Appendix A). In the case of an adsorption measurement, the determination of the dead space volume (V_2, where this equals the volume of the sample cell minus the volume occupied by the sample) is crucial. According to Rouquerol et al [26], this can be performed in one of two general ways: using the *direct* or *indirect* method, where the former involves the measurement of the volume using a gas that is assumed to be non-interacting (typically helium), and the latter involves the subtraction of an estimated sample volume from the measured volume of the empty sample cell. The *excess adsorption*, also known variously as the *surface excess*, *Gibbs' excess* or *Gibbsian Surface Excess* [46-49], is defined as the amount of hydrogen adsorbed beyond that which would be present in the absence of enhanced adsorption (or surface interaction)[10]; the surface excess can also be negative, indicating the presence of a lower density of hydrogen near the surface than would be present in the bulk phase at that particular temperature and pressure.

In the case of the direct measurement of dead space volume, it is assumed that there is no interaction between the helium and the adsorbent surface[11]; however, this is not necessarily the case in micropores and so the measurement must be made at a temperature for which this assumption is valid to an acceptable degree [47,48] (see Section 8.8). For the measured molar uptake or hydrogen content, Δn, to be converted into a wt.% (or mol g^{-1}), the sample mass must be determined accurately. In the case of metallic absorbers this is straightforward, as the sample can simply be weighed before the absorption measurement. In the case of porous adsorbents, it is the degassed sample mass that is required and the presence of atmospheric adsorbates will affect the accuracy of the sample mass measurement. Therefore, a suitable method must be used to determine the value without significant error.

2.1.3 Terminology

This technique has come to be known generally as *volumetric*, but it is also known as the *manometric* technique, or *manometry*, as the sorbed quantity is actually determined from the measurement of a change in pressure, not volume. Early nitrogen adsorption measurements were performed with a mercury burette and manometer, whereby the adsorbed quantity was measured by the change in volume rather than a change in the pressure [26], and so the technique has become known as *volumetric*. In both hydride and adsorption research it is more common to use manometric systems, although there are exceptions. For example, in the hydride field, Gerard et al [50] presented a system that measures the sorbed quantity of hydrogen by measuring variations in the volume of a system at a fixed pressure, although it was designed for the performance of kinetic measurements. However, manometric systems are more common. See, for example, Percheron-Guégan et al [51] and references therein. In the hydride field, volumetric apparatus is also known as *Sieverts' apparatus* [52,53].

---

[10] Assuming that the non-interacting gas within the pores had the same density as the bulk gas phase.

[11] This is also the case in the indirect determination of the dead volume calibration if the density of the material is determined using helium gas pycnometry.

2.2 Examples

Reilly and Wiswall [54] presented a relatively early high pressure system, including their reactor design, which was used for absorption measurements on various binary and ternary hydrides [55,56]. This system was used up to 21.50 atm (2.178 MPa), with the lowest isotherm point around 0.1 atm (10.13 kPa). Early examples of both low pressure and high pressure systems were also described by Blackledge [57]. Bowman et al [58] presented an automated volumetric system that they used for both thermal cycling of AB_5 intermetallics and for isotherm determination. The system is designed for use at ambient temperature and above, and is used up to 500 K. It operates up to 35 atm (3.546 MPa) and is equipped with a pump of base pressure < 10^{-4} torr (13.33 mPa). The lowest pressure point in the presented data is around 0.05 atm (5.066 kPa).

In the field of gas adsorption, a volumetric system designed for the determination of adsorption isotherms was presented by Borghard and co-workers [59]. The system operates in the pressure range 10^{-5} - 1000 torr (1.333 mPa - 133.3 kPa) and at both high temperatures (< 300 ºC) and low temperatures (77 K) . Data are presented for nitrogen adsorption on a porous glass and argon adsorption on faujasite (zeolite). The authors state that their apparatus could be used for hydrogen sorption measurement, although it is only for low pressures. Maglara et al [60] presented a volumetric system designed specifically for the measurement of the adsorption of probe gases on microporous materials at low relative pressures (P/P^0) at low temperatures. Their system was used to perform measurements with nitrogen at 77 K and argon at 77 and 87 K on four types of zeolites, and is again for low pressure measurement. High pressure volumetric adsorption instrumentation was presented recently by Kiyobayashi et al [61]. It operates at a sample temperature of 35 ˚C and up to pressures of 10 MPa, although the system operates only with a rotary pump. Poirier et al [62] recently presented a volumetric system, alongside gravimetric apparatus, which operates using mass flow controllers (MFCs) to determine the amount of gas sorbed by a sample. However, they do not show isotherms produced with either of their systems.

Recent examples of the use of the volumetric technique in hydrogen storage material research include investigations into hydrogen storage on metal-organic frameworks (MOFs) [63-66], conducting polymers [67] and Si-destabilized LiH and MgH_2 [68]. One of the practical advantages of volumetric measurement is its versatility with regard to upper sample size. An example of the use of volumetric instrumentation with a scaled-up reactor bed (in this case, catalysed $NaAlH_4$) is given by Sandrock et al [69] and Gross et al [70].

3 GRAVIMETRIC TECHNIQUES

3.1 Description

The *gravimetric* technique, or *gravimetry*, determines the amount of hydrogen ad- or absorbed by a sample by measuring changes in its mass. The term gravimetry could be used in principle to describe any method that determines changes in a sample by measuring its mass. In this context, however, it means the use of a vacuum microbalance [71] to measure micro- to milligram changes in the mass of a small sample (of the order of grams or less). To measure a sorption isotherm, the sample is exposed to a pressure of hydrogen and its mass monitored until the sample reaches the required 'equilibrium'. To illustrate the principle, Figure 2 shows a schematic diagram of a basic gravimetric set-up. Valves A and B control the hydrogen gas inlet and vacuum outlet, respectively, allowing the control of the hydrogen pressure in the sample (and microbalance) chamber, which is measured using the manometer. The sample is shown sitting in a holder suspended from a microbalance. The diagram implies the use of a beam balance but this can also be a magnetic suspension balance in which the microbalance itself is isolated from the sample chamber [72]. As with the volumetric system, the thermostat or thermal bath can be any temperature-controlling unit and the temperature of the system itself should be carefully controlled. The manometer represents one or more pressure measuring devices, depending on the hydrogen pressure ranges required, in the same way as the volumetric system. The vacuum pump is again generic but it would normally be a UHV-capable system, preferably oil-free. The hydrogen supply should be of very high purity (> 99.999 %) and/or filtered adequately.

To perform a simple, single step experiment on an activated sample in the apparatus shown in Figure 2, valve B is first opened to evacuate the sample/microbalance chamber for a sufficient period. The dry or empty sample mass[12] is then determined from the microbalance reading achieved after this period. Valve A is then opened, allowing the hydrogen pressure in the sample chamber to reach the pressure required for the single isotherm point. As the sample sorbs hydrogen, valve A can then be used to keep the hydrogen pressure in the chamber constant. Once the mass has reached an appropriate 'equilibrium', which could, for example, be defined as a differential mass uptake below a certain threshold [73], the hydrogen uptake can be determined from the sample mass, after the careful application of the buoyancy effect (Archimedes' Principle) corrections [74] and using the dry or empty sample mass as a reference.

To extend this measurement to a full isotherm, the pressure would then be increased again and the mass monitored. After a sufficient period, the uptake can then again be determined from the buoyancy effect-corrected mass, with reference to the dry or empty sample mass. This process is then repeated until a full isotherm has been measured. At each point, the dry or empty sample mass is used as the reference mass,

---

[12] 'Empty' in the sense of unloaded, unhydrogenated, or at the hydrogen loading required at the start of the measurement, including any trapped residual hydrogen.

thus avoiding the accumulative errors inherent in the volumetric measurement procedure.

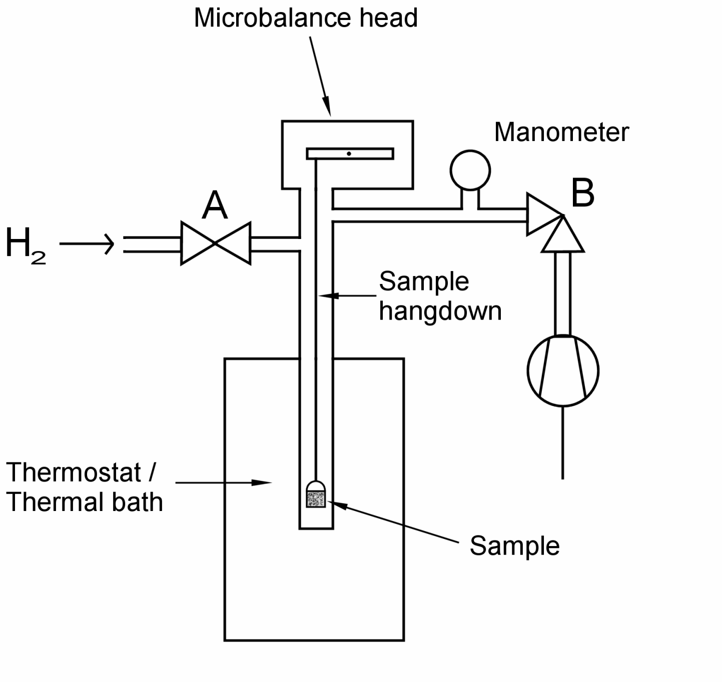


Figure 2. A schematic diagram of gravimetric sorption apparatus.

3.2 Examples

Gravimetric techniques have been more commonly used in adsorption studies on porous materials [75] although some gravimetric hydrogen sorption work has involved the characterisation of hydrides [76-78]. A number of computer-controlled gravimetric systems have been reported in the literature, some of which have been developed for adsorption studies using gases and vapours other than hydrogen; however, as with the volumetric systems mentioned in Section 2, the basic principles and many of the details of operation apply. Rassmussen and Akinc [79] presented an automated system to perform adsorption measurements with various vapours and gases, and tested it by determining sorption isotherms for water and nitrogen on oxide and hydroxide powders. Astill et al [80] presented a system for the automatic measurement of water vapour adsorption, although the system could be used for gases as well and therefore, in principle, hydrogen. A system was developed by Thompson and Fuller [81] for surface area and porosity measurements. This was set up for use with hydrogen, nitrogen, argon and helium, and its operation demonstrated using nitrogen and argon sorption measurements performed on a silica-supported alumina catalyst. A sorption measurement system using a magnetic suspension balance was briefly described by Robens et al [72]. Example measurements were performed using krypton, nitrogen and benzene adsorbed on a graphitic material. A more recent example is the system presented by Akporiaye and Plassen [82] for adsorption studies on micro- and mesoporous materials. However, these systems are all limited to low pressures.

A higher pressure adsorption system was presented by Zuech et al [83] who reported a gravimetric system for adsorption measurements that can operate up to 690 kPa at room temperature and above. The authors performed methane adsorption measurements on a zeolite. Agarwal and Schwarz [73] presented a high pressure system that was used to determine the uptake of several gases on activated carbon up to 60 atm (6.079 MPa) of pressure, both above and below their critical temperatures. De Weireld et al [84] recently developed a system, using a high capacity balance (< 200 g), that can operate up to 10 MPa in the temperature range 303 K to 423 K. It has the unique feature that the entire lower balance chamber is kept at the measurement temperature. Although this restricts the operating temperature range, it reduces problems associated with temperature gradients; however, the primary aim in this case was to prevent the condensation of subcritical adsorbates and so this feature is less relevant for supercritical hydrogen. The instrument also does not offer low pressure operation or high vacuum conditions on the sample for degassing (see Section 7.9). The instrument’s operation was demonstrated by measuring nitrogen and butane isotherms on an activated carbon.

In the hydride field, Lutz et al [85] presented a semi-automated high temperature, high pressure microbalance system for the study of metal hydrides, arguing that the gravimetric technique has certain advantages, including versatility, over the volumetric systems used more widely in metal hydride research. They demonstrated the use of their apparatus by performing absorption and desorption measurements on Mg_2Ni and FeTi. Benham and Ross [86] presented a fully automated system and demonstrated its use by the measurement of hydrogen absorption isotherms on Pd. The system is now available commercially and has been used in a number of recent studies on potential microporous hydrogen storage materials [11], including carbon nanotubes [87], metal-organic frameworks [88-90], zeolites [91,92], activated carbon [93] and microporous polymers [94-98]. A recent study by Furukawa et al [99] used another commercial system, which incorporates a magnetic suspension balance, to determine hydrogen adsorption isotherms for MOF-177 up to a pressure of nearly 80 bars (8 MPa) at 77 K.

4 TEMPERATURE-PROGRAMMED TECHNIQUES

4.1 *Description*

In addition to the two static sorption isotherm determination methods described in the two previous sections, a third type of measurement can be used in the gas phase characterisation of hydrogen storage materials. Temperature-Programmed Desorption (TPD), also known as Thermal Desorption Spectroscopy (TDS), is a well known technique in surface science [100], and is also widely used to study the desorption of adsorbates from porous materials and adsorbents, for applications such as catalysis [101-105]. It is a form of thermal analysis [106], a category that also includes the widely used thermogravimetric analysis/mass spectrometry (TGA-MS) technique [107]. The basic principle is that the sample is heated in a controlled manner and the quantity of hydrogen released is monitored. This can be carried out in a number of ways, including the measurement of the pressure in a fixed volume [108], through the use of a mass flow meter [109] or by monitoring the evolved hydrogen using a mass spectrometer [110], in the same way as in a TGA-MS system. The use of a mass spectrometer allows evolved gas analysis (EGA), so that other evolved species can be identified, if appropriate, whereas the other two methods are non-selective. Hydrogen TPD is also used to determine the hydrogen content of steels and other alloys [111-113] in the study of hydrogen embrittlement phenomena.

To illustrate the principle, Figure 3 shows a schematic diagram of a TPD set-up, which can operate in three configurations. In contrast to the diagrams in Figures 1 and 2, not all components are essential; however, they have been included to illustrate the different ways in which TPD can be implemented. The system shown can operate (i) in a flowing mode, using the mass spectrometer to determine the desorbed quantity of hydrogen, or in a static (non-flowing) mode using either (ii) the mass spectrometer or (iii) the manometer to monitor the desorbed quantity of hydrogen. Hydrogen and helium supplies (very high purity and/or filtered) are shown on the left, with the flow from each controlled through mass flow controllers (MFC1 and MFC2). Valves A and B control the gas inlet to the sample cell and the vacuum outlet, respectively. Valve C allows the gas to flow through the exhaust and valve D allows the generic vacuum pump to evacuate either the volume between valves B and C, or the sample cell, if required. The sample sits in a cell in the temperature control unit, which can be any system that allows a controlled linear temperature ramp to be applied to the sample in the required temperature range. A temperature sensor (not indicated in the diagram) should be positioned either near or in contact with the sample. The manometer represents one or more pressure measuring devices, depending on the hydrogen pressure range required and the configuration in which the system would be operated. The mass spectrometer (MS) is positioned after valve B, with a heated capillary connecting it to the system [114]. The vacuum pump connected via valve D is not necessarily the same as the one required for the MS, and the exhaust can either be an outlet straight to atmosphere or a connection to an oil-free pump, depending on the operation of the system.

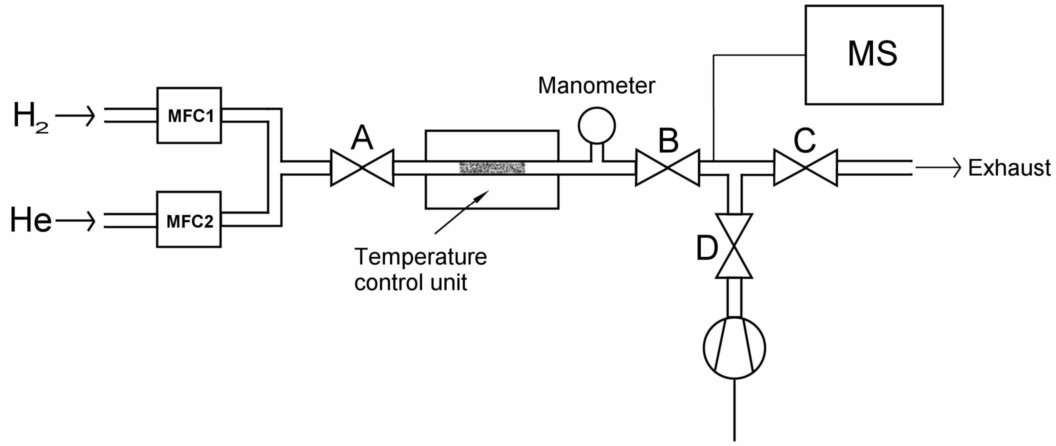


Figure 3. A schematic diagram of thermal desorption spectroscopy apparatus.

For the sake of clarity, we shall assume that the system is initially loaded with a hydrogenated sample held at ambient temperature at which there is minimal hydrogen desorption, so that the hydrogen can be considered to be thermodynamically or kinetically trapped in the sample. A simple TPD experiment could then be performed in one of three ways:

4.1.1 Flowing mode, using MS

With valve D closed, valves A, B and C are fully opened and helium is flowed through the system at atmospheric pressure using MFC2. The hydrogen signal from the MS is then monitored while the temperature control unit increases the sample temperature from ambient to the selected upper temperature of the experiment. After the thermal desorption, a calibration measurement is performed either by using a calibration sample of known composition [110] or, alternatively, by flowing a known quantity of hydrogen through the system using MFC1.

4.1.2 Static mode, using MS

With valves A and C closed, and valves B and D open, the system is evacuated for a suitable period[13]. The hydrogen signal from the MS is then monitored while the temperature control unit increases the sample temperature from ambient to the selected upper temperature of the experiment. A calibration measurement is then performed using a sample of known composition [110].

4.1.3 Static mode, using manometer

With valves A and C closed, and valves B and D open, the system is evacuated for a suitable period. Valve D is then closed. The temperature control unit then increases the sample temperature from ambient to the selected upper temperature of the

---

[13] This is different to degassing a microporous adsorbent, as in this case the sample is already loaded with hydrogen.

experiment while the manometer is monitored as a function of time. In this case, the total desorbed quantity of hydrogen can be determined volumetrically from the known volume of the system and so there is no need for a calibration measurement. A variation on this configuration is the use of a flow meter, which would prevent the build-up of a back pressure in the volume between valves A, C and D, but may reduce the accuracy of the calculated desorbed quantity.

In each case, very careful attention must be paid to the selection of temperature ramp rates, with measurements performed at a number of rates to confirm that this does not have a significant effect on the calculated desorbed quantity. The system shown in Figure 3 also allows the hydrogenation of the sample before the determination of a desorption spectrum. To hydrogenate the sample in this system, with valves A and C closed, valves B and D open and the MS isolated, the sample should be degassed for a sufficient period and then taken to a temperature suitable for hydrogenation. Valve D is then closed, before hydrogen is flowed through MFC1 and into the sample chamber. Once a sufficient amount of hydrogen has been put into the sample chamber, up to the required pressure, valve A can be closed and the temperature dropped to a level that thermodynamically or kinetically traps the hydrogen. If this hydrogenation process is not, or cannot be, carried out *in-situ*, the sample must be loaded into the system already hydrogenated. However, this is not appropriate for all materials. If a glovebox is available for sample transfer, either through the use of a specially constructed sample cell or by mounting the instrument itself in a glovebox, then mounting a hydrogenated sample is feasible for a range of hydride samples. For porous adsorbents, on the other hand, the hydrogen adsorption process would have to take place *in-situ*, which in turn would require low temperature operation [105,115].

The hydrogen signal (or pressure/flow) against time data produced from a TPD experiment can be used in one of two general ways. Firstly, the spectrum produced can be analysed in terms of peak positions or, secondly, an integration under the spectrum will give a total desorbed quantity. Attempts have also been made to model the kinetics of temperature-programmed desorption from elemental hydrides [116-118].

4.2 Examples

There have been a number of reports in the literature of the use of TPD to study hydrides [108-110,116-124] and a number of recent articles on potential hydrogen storage materials have used a form of the technique, although not always quantitatively. Mendelsohn and Gruen [120] published one of the early reports of the use of TPD to study bulk metal hydride samples. They performed TPD on two AB_2 compounds ($ZrV_{1.6}Fe_{0.4}$ and $ZrV_{1.2}Cr_{0.8}$) between ambient temperature and 700ºC, and monitored the desorbed hydrogen by measuring the hydrogen pressure. The desorption was, however, performed into vacuum to determine characteristic desorption temperatures rather than to quantify the desorbed hydrogen. The measurements were possible in this temperature range because of the high stability (high standard decomposition temperature) of the hydride compounds being studied. Around the same time, Stern and co-workers [108] also published thermal desorption spectra from another AB_2 compound (ZrV_2). This group subsequently published further results on a number of metallic hydrogen absorbers, including HfV_2 [119], Pd

[121] and $LaNi_5$ [122]. More recently, Hall and co-workers [123] studied hydrogen desorption from a FeTi thin film sample loaded electrochemically. This was performed using standard thermogravimetric apparatus under a flow of argon. In their presentation of TDS apparatus, Castro and Meyer [109] show desorption data from Pd. Palladium hydride was also used by Fernández et al [124] to demonstrate the operation of their combined differential scanning calorimetry (DSC) and TDS apparatus, along with hydrides of Ti, $TiCr_{1.85}$ and $ZrCr_2$. Also of relevance are reports on the quantitative calibration of mass spectrometer signals in the literature. For example, Maciejewski and Baiker [125] looked at the calibration of the mass spectrometer signal from a thermal analyzer that offers combined thermogravimetry and differential thermal analysis, and Kaisersberger and Post [126] covered the practical aspects of the coupling of mass spectrometers to thermal analysis instrumentation.

A number of recent reports of hydrogen storage using complex hydrides have used a form of the technique [9,127,128]. For microporous materials, however, the use of the technique in the quantitative determination of desorbed gaseous hydrogen is not so well established. Dillon et al [129] used the technique in their widely criticized work [130] reporting the high potential room temperature hydrogen storage capacity of carbon nanotubes (see Section 6.1 and Footnote 14) and Hirscher et al [131] used it in their subsequent investigation. The measurements made in the latter case were high temperature (> 300 K) and the data more closely resemble the mass spectrometer signal seen during the degassing of activated carbon samples, due to surface decomposition [132], than the desorption spectra seen during the thermal desorption of other gaseous adsorbates during low temperature TPD [105]. Züttel et al [133] used a form of the technique to show that hydrogen desorption from a series of carbons was the result of the decomposition of hydrocarbons formed during above ambient temperature hydrogenation of the samples, rather than to quantify the release of adsorbed gaseous hydrogen. Panella et al [115], however, have recently reported apparatus for the low temperature desorption of adsorbed molecular hydrogen from single-walled carbon nanotubes and activated carbon, in the range 20 - 500 K.

5 PRACTICAL CONSIDERATIONS

There are many practical considerations involved in the choice of sorption instrument or technique. The latter sections of this report focus on the specific issue of accuracy; however, although this is important, it might not necessarily be the main priority. For example, if the purpose of measurement is new materials discovery, then sample throughput may be more important, providing the material's sorption properties can be determined to sufficient accuracy during this process. If gas phase measurements are being performed to demonstrate the practical use of a material in a prototype store, then a suitably modified volumetric device can be used [69,70], and can give sufficiently accurate results; however, it would not be reasonable to analyse the results in terms of the nature of the sorption process, the microstructural changes that are occurring, and so on. The following is therefore a brief discussion of some of the points worth consideration.

5.1 Cost

Cost is obviously a very practical consideration for many and may impose the most restrictions on instrument choice. A direct comparison of suppliers and their instruments is not the intention here but, considering only hardware costs, in ascending price order, the author would categorise the options as, firstly, a self-constructed volumetric or (non-EGA) TPD device, secondly, a self-constructed gravimetric system, thirdly, commercial volumetric and gravimetric instruments, followed by commercial TPD/gravimetric instrumentation equipped with mass spectrometry. Keller and Robens [24] state that gravimetric apparatus is more expensive because of the cost of the microbalance and this would seem, in principle, reasonable; however, for specialised commercial high pressure hydrogen sorption equipment, this is not necessarily the case.

The use of EGA (using mass spectrometry) can introduce significant additional cost. The need for EGA depends on the material type. The study of hydrogen sorption in thermally stable intermetallics does not typically require EGA. However, if hydrogen release occurs close to the sublimation temperature of the host solid or there is a chance of, for example, ammonia evolution occurring at the temperature at which the desorption is being performed (as is the case with nitrides [127]) then EGA may be required. EGA may also be useful to monitor the degassing process.

5.2 Ease-of-use

Volumetric systems are, in general, easier to use, in terms of sample loading. Gravimetric systems require a sample to be loaded on to the balance. This should not cause any significant problems, although it can complicate inert gas environment sample handling. The ease-of-use of temperature-programmed techniques depends on the instrument configuration. In principle, however, for any of the configurations illustrated in Figure 3, sample loading is the same as for volumetry. The development and operation of instrumentation utilizing EGA requires a good understanding of the practical application of mass spectrometry [114,126].

5.3 Measurement Times

Volumetric measurements will generally be quicker than gravimetric measurements, for a given material type. Measurement times depend so much on the instrument, the material type and its kinetic uptake behaviour, the preparation requirements and the choice of parameters (for example, number of equilibrium points in an isotherm) that it would be misleading to state exact figures. However, as a very rough guide for realistic measurement times, a single TPD spectrum could be obtained in a day, as could a volumetrically-determined (automated) sorption/desorption isotherm for a material with relatively rapid kinetics, whereas a gravimetrically-determined isotherm is likely to take longer than a day. This excludes any activation, pretreatment or degassing that may be required. Depending on the aim of the experiment, it is also possible for a gravimetric sorption measurement to take weeks or months.

5.4 General Versatility

The highest accuracy is most likely to be achieved by developing instrumentation for a very specific purpose; however, this may restrict the versatility of the instrument, which could be an important consideration. Besides the measurement of an isotherm, or a thermal desorption spectrum in the case of temperature-programmed techniques, it may be necessary for an instrument to perform one or more additional tasks. Two prime examples are *activation* and *long term cycling*. As touched upon earlier in this report, *activation* is the process by which a material is prepared for hydrogen sorption and it can take many forms. In microporous adsorbents, it is the part of the procedure in which the surface is cleaned in preparation for hydrogen sorption and may involve the removal of solvent still present from the synthesis process or the degassing of the sample to remove environmental adsorbates, principally from the internal pores. In hydrides, it can involve an extended process of sample degassing, exposure to a pressure of hydrogen, perhaps at an elevated temperature, followed by a series of hydrogenation cycles, and so on. The *long term cycling stability* of a material is an important factor in its suitability as a candidate for a practical hydrogen store, although it is an issue of more relevance to hydrides, than to microporous adsorbents. It can be tested by first measuring a sorption/desorption isotherm, then cycling the material using repeated hydrogenation/dehydrogenation cycles, followed by further measurement of an isotherm. Differences in the isotherms before and after the extended hydrogen cycling will then give valuable information on the consequences of the cycling process, and hence the long term cycling stability of the material. The hydrogen cycling can be performed either by thermal or pressure-induced methods. In terms of hydrides, if the cycling is not to be performed in separate cycling apparatus [134,135], both of these processes are probably better performed in volumetric, rather than gravimetric, apparatus; unless a material-specific question that favours the gravimetric technique is being addressed [78]. However, in the case of microporous adsorbents, it can be argued that gravimetric apparatus is better for sample degassing, and hence *activation*, because high vacuum conditions on the sample are more readily achieved and the sample mass can be carefully monitored throughout the degassing process; although a microbalance of smaller capacity will also limit the amount of material that can be activated in one batch. A third, although perhaps less prominent, example is the study of the effects of *gaseous impurity contamination* on the storage performance of a material. This can be studied either using pre-prepared gas mixtures or by mixing gases using the instrument itself, which would therefore require multiple MFCs. The versatility of an instrument also includes the issues addressed in the following three sections.

5.5 Sample Size

In principle, in the volumetric technique, the upper sample size (mass and volume) is unlimited, whereas in gravimetry it is limited by the balance capacity, which, depending on the sensitivity and long term stability required (and the balance type), can vary from below a gram, up to 200 g [71,84]. However, in reality, the sample size in a volumetric instrument will be restricted by the size of the calibrated volume, or volumes, in the system and the sample cell itself. The minimum sample size is difficult to define, although there are definitely limits to the lower sample size in volumetric measurements, which tend to be performed on larger samples. To determine a wt.%, or μmol g^{-1}, uptake the initial mass of the sample must be determined to sufficient accuracy (see Section 7.6), which will be limited in volumetric measurement by the accuracy of the balance used to determine the sample mass. In addition, there is also the mass loss that occurs during the degassing process. Sample size, therefore, can have important implications on the accuracy of a measurement (see Section 7). In principle, the use of a mass spectrometer for TPD should allow the use of very small sample sizes, as the detection limits for a quadrupole mass spectrometer, particularly one equipped with a secondary electron multiplier (SEM), are very low. In addition, the use of small samples limits heat transfer problems during thermal ramping; however, accurate sample mass determination still restricts the lowest sample size.

5.6 Pressure and Temperature Ranges

There are no clear rules with regard to which techniques may be better in different regimes, although the volumetric technique has been more commonly used in higher temperature hydride research and is undoubtedly more suitable for very high pressure measurements (greater than the range of interest for storage applications [136]). At higher temperatures the microbalance in gravimetric systems is subjected to increasing thermal disturbances, which increase with increasing pressure; and, at high pressures, the buoyancy effect correction becomes more significant and will therefore have a larger effect on the calculation of the sorbed quantity. Conversely, high vacuum conditions are more easily achieved in a vacuum microbalance and therefore gravimetry may be more appropriate for measurements requiring low pressures (or initial high vacuum conditions). The benefits of high vacuum degassing conditions may be counter-balanced somewhat by the effects of thermomolecular flow (thermal transpiration) on the balance reading at very low pressures (see Section 7.13). However, these latter points are closely related to accuracy.

Practically, the pressure and temperature ranges are restricted by the instrument design, rather than the technique. Restrictions are placed on instrumentation by the upper operating temperatures and pressures of individual components. In some of the earlier microbalance systems [80], for example, glass was used thus limiting their operation to ambient pressure. However, stainless steel has an upper operating temperature of approximately 500°C and with hydrogen, at these higher temperatures, there are also pressure limitations, as hydrogen permeation rates increase greatly with increasing temperature [137,138]. Above 500°C, quartz can be used but this limits the pressure again to ambient. Another restriction is due to the specification of the valves in the system. This can restrict both the upper operating pressure and the achievable vacuum in a system. The choice of fittings also has a significant impact. The use of UHV-capable fittings can limit the upper operating pressure of a system, and, conversely, the use of high pressure components can limit the achievable vacuum. It is practical issues such as these that primarily distinguish low pressure apparatus for the measurement of the adsorption of gases other than hydrogen (for example, nitrogen and argon) from specific hydrogen sorption instrumentation.

5.7 Material Type

A number of the issues relating to measurements on different material types have been addressed specifically in the previous sections, but the main points to consider are: (i) the pressure and temperature range of interest; (ii) the activation requirements; and (iii) the sample handling requirements.

6 MEASUREMENT ACCURACY

6.1 Introduction

Following the introduction to the measurement techniques given earlier, we will now focus on their accuracy. This issue came to prominence recently due to the controversy over the storage properties of carbon nanostructures, during which widely varying claims of potential storage capacity and hydrogen uptake behaviour were made. The controversy followed initial reports of possible room temperature hydrogen storage of up to 10 wt. % in single walled carbon nanotubes [129] and subsequent claims of up to 67.55 wt. % uptake by graphite nanofibres [139]. The claims in these initial studies, in particular the work on nanofibres, were met with scepticism [4,5], due in part to the unlikely claimed capacities (an uptake of 67.55 wt. %, for example, equates to a hydrogen-to-carbon atomic ratio (H/C) of over 24). Subsequent studies of the sorption of hydrogen by various carbon nanostructures then produced a range of conflicting results. Critical reviews of the initial work, and some of the studies that followed, were later published by Züttel and Orimo [130], Hirscher et al [131] and Becher et al [140], and a number of other articles on the subject can be found in the literature. See, for example, the review by Lamari Darkrim et al [141], which includes tabulated data summarizing the range of values reported in the literature at the time. The problems appear to have been caused, primarily, by insufficient microstructural materials characterisation of the samples, as well as a lack of care taken in the experimental work used to determine their storage capacity[14], and the latter undoubtedly contributed to some of the more extravagant claims.

The intention of the latter part of this report is to provide an overview of work that has specifically focused on the accuracy of gas phase hydrogen sorption measurements, including any relevant existing guidelines or standards, and to give a balanced discussion of the various possible error sources, with regard to each technique and with reference to relevant literature. In addition, some relevant work on accuracy in the measurement of the adsorption of gases other than hydrogen is covered. This part

---

[14] One of the questionable aspects of the work by Dillon et al [129] was the calculation, or estimate, of the total potential hydrogen uptake. This was performed by extrapolating an approximate measured hydrogen uptake of 0.01 wt.% by a 1 mg sample that was estimated to consist of only 0.1 to 0.2 wt.% of pure single-walled nanotubes. The uptake of 0.01 wt.%, which was determined using TPD, was assumed to be due only to sorption on the nanotubes, thus giving an uptake on pure single-walled nanotubes of between 5 - 10 wt.%. Therefore, the approximate 0.01 wt.% hydrogen uptake was attributed only to single walled nanotubes, even though the remainder of the sample was a poorly characterized soot, which itself could interact with hydrogen. Chambers et al [139] used self-constructed volumetric apparatus to measure their extraordinary hydrogen uptakes. An immediately evident problem with their sorption data was the inconsistent variation in the uptake determined for other well-known materials, which included particularly high wt.% uptake values for Pd and graphite, and a particularly low value for $LaNi_5$. Values for hydrogen absorption and desorption by $MnNi_{4.5}Al_{0.5}$ were also quoted, although presumably the authors meant $MmNi_{4.5}Al_{0.5}$ (where Mm is a mischmetal) [142], and in this case the absorption value was also remarkably high. Such inconsistencies and anomalies should have helped identify problems with their measurement method, but they appear to have been overlooked by both the authors and the reviewers.

of the report is based on a recent article published in the International Journal of Hydrogen Energy [2].

Firstly, to clarify, we shall give definitions of common terms that have specific meanings [143,144] but are sometimes used interchangeably. *Repeatability* is the closeness of the agreement between the results of successive measurements carried out under the same conditions of measurement. The *reproducibility* is the closeness of the agreement between the results of measurements carried out under changed conditions, and the *accuracy* of the instrument, or a particular measurement, is the ability of the instrument, or the measurement, to give a value close to the true value. As the true value can never really be known, under this definition, accuracy is qualitative and, although it can be 'high' or 'low', it cannot have a specific value. The quantitative equivalent is the *uncertainty* of the measurement [145]. The conditions can include the procedure, observer, instrument, experimental conditions and location. So, in the context of sorption measurements, repeatability is the closeness of agreement between measurements made in the same way, on the same sample, on the same instrument, in the same place by the same experimentalist, whereas reproducibility is the closeness of agreement between measurements made with any of these factors changed. In practical terms, this report will use repeatability to mean the results of successive measurements made using the same technique on samples from the same batch, in the same laboratory, whereas reproducibility will mean the results of successive measurements performed using either different techniques or instruments, or performed at different laboratories. Repeatability is easily determined in a single laboratory by a single researcher, whereas reproducibility tends to require Round Robin-type exercises [146], depending on how well a single laboratory is equipped[15]. Good repeatability is certainly not an automatic indicator of high accuracy, as it can easily be observed for a series of measurements that consistently under- or overestimate the storage capacity of a material. There is also likely to be an underlying uncertainty in the 'hydrogen storage capacity' of a material, particularly with so many variables involved in a single measurement, and so it is reasonable to expect a certain spread of values, particularly when testing reproducibility. For example, even for palladium, one of the most extensively studied and well known hydrogen-absorbing materials [147,148], there is a difference between the hydrogen uptake in poly- and nanocrystalline samples [149-152] and so a palladium sample's uptake will have an uncertainty associated with its degree of crystallinity (or grain size)[16].

The primary aim of the investigation of measurement accuracy, in the context of hydrogen sorption measurement, is to separate experimental artefacts from real

---

[15] Although testing reproducibility in a single laboratory does not take account of possible geographical differences, such as the exposure of samples to different air humidities.

[16] The argument being that the smaller the grain size, the greater the proportion of grain boundaries. The grain boundaries can be considered as a secondary phase that shows different uptake behaviour to the grains themselves, and therefore a nanocrystalline sample consisting of a larger proportion of this secondary phase will show different uptake behaviour to a sample with a smaller proportion. However, the gas phase measurement of the difference could potentially be susceptible to experimental artefacts if the grain boundaries, as a secondary phase, are not defined sufficiently. In addition, impurity levels are likely to add an additional amount of uncertainty: the presence of additional elements in a host metal will affect the hydriding properties, and so, in principle, if there are different impurities present, or different impurity levels, in two samples there will be a difference in their hydrogen absorption properties.

material behaviour, or the real (or true) hydrogen uptake of a material, in order to help ensure that under or over-estimated uptakes are not measured as a result of a poor experimental set-up or procedure, poorly applied corrections or incorrect assumptions. This applies equally to modified, or treated, forms of existing materials, as well as newly discovered materials or compounds. A crucial part of the accurate determination of the hydrogen storage capabilities of new or existing materials involves the adequate microstructural characterisation of samples[17]. Although the microstructural characterisation of potential storage materials is not the subject of this report, it is important to note that a certain amount of information is required before accurate characterisation of the hydrogen sorption properties of a sample can be carried out; one aspect, for example, being the chemical density of the sample in its activated state. Any uncertainty in this value will be carried over into the sorption measurement. Aside from the controversy over carbon nanotubes and nanofibres, there are therefore additional arguments for the further investigation of the accuracy of the gas phase measurements routinely used to characterise the hydrogen sorption properties of materials. Firstly, there has been an increase in the amount of research focused on nanocrystalline or amorphous materials as potential storage media [153]. Secondly, as a natural consequence of the search for new storage materials of high gravimetric hydrogen storage density, measurements are increasingly focused on low density and microporous host materials.

With regard to the first point, there is little doubt that the reversible ‘hydrogen storage capacities’ of a large number of binary and ternary metal hydrides have been determined to a high accuracy through years of extensive research using a range of techniques [14-19], together with accompanying theory and modelling. The hydrogen stoichiometries, and hence both the volumetric and gravimetric storage capacities, in intermetallic compounds, for example, appear to be limited by the empirical Westlake criterion that specifies a minimum allowable H-H distance of 2.1 Å, along with a minimum interstitial hole radius of 0.4 Å [154]. Anomalous results, in terms of storage capacity, will therefore be relatively obvious and can be investigated further. Also, hydrides formed from crystalline single phase materials are relatively easy to study using neutrons and X-rays. For example, the *in-situ* powder diffraction techniques that are now available allow the absorption to be monitored [128,155], so that the hydrogen stoichiometry can be directly related to the corresponding lattice expansion, phase transitions, and so on, through the absorption process, even at relatively high hydrogen pressures. The hydrogen absorption process can therefore be observed, or the hydrogen ‘seen’ to a certain extent. Briefly returning to Pd, Mütschele and Kirchheim [149,150] measured the hydrogen uptake by polycrystalline (average grain diameter of 20 μm) and nanocrystalline (average grain diameter of 8 nm) samples electrochemically at low hydrogen content. The grain size of the nanocrystalline sample, in this case, was determined using both transmission electron microscopy (TEM) and x-ray powder diffraction peak broadening analysis [156], with the results from both techniques in reasonable agreement. In this case, there is only one phase, apart from the grain boundaries, and there are no chemical compositional gradients within the sample, no catalytic additives of different bulk (or chemical) density and it does not have a high surface area, which may lead to a greater build-up of surface oxides. Inhomogeneous samples that contain multiple phases, compositional gradients, and so on, are difficult to characterise microstructurally and

---

[17] For example, avoiding an over reliance on laboratory x-ray powder diffraction.

therefore hydrogen sorption measurements on them may be more susceptible to certain sources of error. In addition, the hydrogen absorption process cannot be observed in the same manner as chemically homogeneous, crystalline materials. The important point is that gas phase sorption measurements should be performed accurately so that experimental artefacts do not lead to mistaken conclusions about the effects of particular treatments or synthesis techniques.

In hydrogen adsorption on microporous adsorbents it is also not possible to ‘see’ the adsorbed hydrogen unless the samples are at very low temperatures [34,157,158] and, therefore, not in a practical storage situation[18]. The material type again has a significant influence on the likelihood of the accurate determination of a real reversible hydrogen storage capacity. Zeolites [91,92] and metal-organic frameworks (MOFs) [88-90,159,160], for example, are crystalline microporous materials with a well-defined pore structure that can therefore be characterised (crystallographically) relatively easily, unlike activated carbon, carbon nanotubes and the like. In addition, the reactivity of the surface of such carbon materials appears to make their sorption properties more dependent on a number of other factors, including storage conditions and degassing procedures. Adsorption methods [39,161] using inert probe gases are relied upon, to a certain extent, to characterise the porosity of materials that do not have a regular network of pores defined by the crystallography of the structure and, therefore, do not perhaps provide such a rigorous test of the likely accuracy of a measured hydrogen uptake. Although there are more sophisticated analysis methods that go beyond the measurement of a simple adsorbed quantity [26,28,46,162] there is still a strong reliance on the accurate determination of the excess adsorption (Gibbs excess). An example of a possible error source that could affect both hydrogen and non-hydrogen adsorption measurements is the assumption that helium does not adsorb [46-49] during either density determination measurements or the dead space volume calibration for the volumetric method.

This last point leads us to the second argument: that low density hosts, whether adsorbents or hydrides, may be affected more by some error sources than more dense host materials such as Pd and $LaNi_5$[19]. A recent study by Blach and Gray [53] has demonstrated the extent to which uncertainty in a material’s chemical density can affect the volumetric measurement of hydrogen uptake by the sample (see Section 7.8). Combined with microstructural sample characterisation difficulties, or ill-defined samples, this could lead to increased uncertainty in measurements and, therefore, even more care should be taken to ensure that experimental artefacts do not affect the results significantly. The investigation of the relative importance of error sources, in the context of storage applications, is therefore important and any further research that may lead to a clearer understanding of the effects of the various error sources would, in the author’s opinion, be valuable. So, within this context, we will now review previous work relating to the accuracy of gas phase hydrogen sorption

---

[18] References [34] and [157] describe the use of both neutron diffraction and neutron spectroscopy to directly probe adsorbed molecular hydrogen (or deuterium in the case of the former) in metal-organic frameworks (MOFs) at temperatures of 3.5 K and in the range 60 – 100 K, respectively. A number of other examples of similar work are given by Neumann [158].

[19] In gravimetric and volumetric measurements, the buoyancy effect and dead space volume corrections, respectively, increase with decreasing host structure density for a given sample mass and so each technique is more sensitive to the measured or assumed sample density with lower density samples.

measurements, including some comparative studies, together with some relevant standards and related guidelines. In the following section, the potential sources of error in sorption measurements performed volumetrically and gravimetrically will be discussed, together with those related to temperature-programmed desorption (TPD).

6.2 Previous Work

There is a vast quantity of published literature available on hydrogen-sorbing materials and their properties[20]. Over the last 30 years or so, however, probably the largest amount of work, in terms of the determination of the bulk hydrogen sorption properties of materials, has been carried out on the intermetallic hydrides. This is primarily due to their use as nickel-metal hydride (Ni-MH) battery electrode materials [21-23]. As a consequence of this practical application, a number of Japanese Industrial Standards (JIS) [44,163-166] exist that relate to the determination of the properties of these materials. Unfortunately, these standards are quite limited in terms of their application to other hydrogen storage materials. For example, JIS H 7201-1991 [163], which describes the measurement of pressure-composition-temperature (PCT) relations, refers specifically to hydrogen absorbing alloys with a plateau pressure of 0.1 to 2 MPa at room temperature to 150 ºC. It also refers only to the use of the Sieverts method and therefore excludes the use of the gravimetric technique for the measurement of pressure-composition isotherms (PCIs). JIS H 7202-1993 [164], a standard on hydriding rate determination, refers to the measurement of the hydriding rate of hydrogen-absorbing alloys at standard decomposition temperatures between 250 and 400 K (see Section 1 and Footnote 6).

The determination of the gas adsorption properties of porous materials [26,40] is also a mature field and recently, following the intense interest in the use of carbon nanotubes as a storage medium, other microporous materials have been attracting attention [11], with examples including metal-organic frameworks (MOFs) [88-90,159,160] and microporous polymers [94-98]. There are IUPAC guidelines [27] that include a check list to help in the measurement of adsorption isotherms, many points of which are applicable to the case of hydrogen sorption. The guidelines as a whole apply to materials across a range of porosities, from micro (pore width, $p_w < 2$ nm) to macroporous ($p_w > 50$ nm), rather than just the microporous materials of interest for adsorptive hydrogen storage[21]. The guidelines also describe the gravimetric and volumetric techniques and cover degassing procedure (see Section 7.9). They also state that they are not applicable to the case where chemisorption occurs, and so apply, in our area of interest, specifically to the measurement of the adsorption of molecular hydrogen. The issues outlined are discussed in more detail by Rouquerol et al [26]; although they do not cover hydrogen adsorption specifically, much of the practical advice and information is applicable. They concentrate primarily, however, on lower pressure adsorption measurements. The IUPAC guidelines were later used as a basis for a standard on the BET method of specific surface area determination [167]. More recently, Belmabkhout et al [168] published a

---

[20] The history of the study of metal-hydrogen systems goes back to 1866, when Thomas Graham first discovered the absorption of hydrogen by palladium [147].

[21] The microporous category can be broken down further into ultramicroporous ($p_w < 0.7$ nm) and supermicroporous (0.7 nm $> p_w >$ 2 nm) [94,161], of which potential hydrogen storage materials are most likely to be the former.

comparative study of volumetrically and gravimetrically determined supercritical nitrogen adsorption isotherms measured on an activated carbon and discussed a number of the issues surrounding the accuracy of these types of measurements. A recent monograph by Keller and Staudt [40] also includes significant discussions of issues surrounding the accuracy of the measurement of the adsorption of gases other than hydrogen, although it focuses on the measurement of multi-component gas adsorption equilibria and the measurement of gas adsorption under (industrial) conditions unsuitable for hydrogen adsorption measurement[22].

Returning to hydrides, in an article specifically on the accuracy of gas phase sorption measurements, Wang and Suda [169] outline the most important considerations in determining the isothermal absorption kinetics of intermetallic hydrides. They give an excellent example of the problem of the poor reproducibility of results from bulk hydrogen storage material characterisation, although we would not necessarily expect the results of the measurement of equilibrium properties to vary as much. It is also specific to AB_5 hydrides (or, at least, intermetallic hydrides) rather than hydrogen storage compounds as a whole. They classified the sources of error in kinetic measurements of this type as: (1) the thermal effects caused by the heat of reaction, (2) the system volume to sample mass ratio, (3) the sample history, (4) the experimental conditions, (5) the particle surface state and (6) the particle size. Although the intention of the article is the reduction of errors in isothermal kinetic measurements, the points identified are also applicable to a certain extent in equilibrium uptake measurements. The significance of various error sources in both the volumetric and gravimetric techniques in the accurate determination of equilibrium sorption isotherms for $LaNi_5$ was addressed in detail in a series of articles by Gray and co-workers [77,78,170-172].

More recently, there has been some work on hydrogen adsorption measurement accuracy prompted by the interest in carbon nanostructures. Kiyobayashi et al [61] published work on the accurate measurement of carbonaceous materials, describing volumetric apparatus designed to make accurate measurements on activated carbons and nanofibres. Zhang et al [173] also recently published work on the accurate determination of hydrogen uptake in carbonaceous materials. Like Kiyobayashi and co-workers [61], they describe their volumetric apparatus but do not compare the results from their measurements with those from other instruments. In fact, they comment on the significant difference in the uptake rates from their samples compared with similar studies. However, they concentrate on the importance of the careful processing of experimental data and make an important point about the use of equations of state (EOS) other than the ideal gas law when performing calculations with hydrogen at higher pressures (< 1 MPa). The issue of the use of alternative EOS was also examined by Zhou and Zhou [175], and by Zhou et al [66] in their recent volumetric study of hydrogen and methane adsorption in MOF5 and ZIF8 (see Section 7.12). Tibbetts et al [176] discuss possible sources of error in volumetric hydrogen sorption measurements in their paper on hydrogen sorption in carbon materials, suggesting that the main problems are leaks and temperature variations due to both room temperature fluctuations and the pressurization of the volumes in the system. Becher et al [140] reviewed previous work on hydrogen adsorption on carbon

---

[22] The determination of adsorption equilibria for gas separation processes is emphasized and degassing conditions are described as vacuum below 15 Pa (see Section 7.9).

nanotubes and comment on the sources of error in this type of measurement. In another paper, Hirscher et al [176] discuss the accuracy of sorption measurements but concentrate on temperature-programmed desorption (TPD). A comparative study was published by Ansón and co-workers [87], in which they performed measurements on single walled carbon nanotubes using three different techniques: two gas phase and one electrochemical. They comment in their introduction on the difficulty of finding agreement between adsorption data using different techniques, although this is specifically in reference to carbon nanostructures. Their volumetric and gravimetric results show reasonable agreement, in that they both show relatively low hydrogen uptakes; however, they are plotted on different scales and so are difficult to compare. Blackman et al [177] presented a differential pressure volumetric system for the accurate determination of hydrogen uptake in carbon materials, and Lee et al [178] recently reported accurate volumetric measurements on very small carbon samples (see Section 7.6).

In a recent paper, Furukawa et al [99] propose MOF-177 as a benchmark hydrogen adsorption material and show comparative data measured using gravimetric and volumetric instrumentation. Their data demonstrate good reversibility, which is indicative of physisorption, and the gravimetric and volumetric uptakes show good quantitative agreement; however, the saturation pressure of the excess adsorption differs in each case. In addition to Gibbs excess adsorption they also show total uptake although, as the authors explain, this is only an estimate of this quantity and does not necessarily represent a true uptake (see Appendix A).

7 SOURCES OF ERROR AND EXPERIMENTAL CONSIDERATIONS

In this section we consider some of the possible sources of error and discuss them in the context of the standards and guidelines referenced in the previous section, as well as recent literature. Although it is difficult to quantify the importance of each source of error, it is clear that some are not relevant for certain types of measurement. The discussion will focus on the volumetric and gravimetric techniques, but temperature-programmed techniques will be considered where appropriate. Comments will also be made on issues that may be particularly important in assessing the reproducibility of hydrogen sorption measurements, in terms of the measurement of the properties of the same material using different instrumentation.

There are a number of levels on which one may wish to examine the accuracy of a sorption measurement. Firstly, there are measurements to determine whether a material will (reversibly) sorb hydrogen and, if so, approximately how much. Secondly, there are measurements to further investigate the sorption properties of a material already known to (reversibly) sorb hydrogen. This may, in the case of hydrides, for example, include the production of a van ’t Hoff plot [4]. Thirdly, there are highly accurate measurements in which the isotherm is intended to reveal detailed information on the type of sorption taking place. The nanotube controversy triggered the need to look at the first type of measurement for which some of the error sources covered here are unlikely to be relevant; for example, thermal transpiration effect corrections at low hydrogen pressures. This type of measurement is required for new materials discovery. The second type is common and is perhaps closer to what might be regarded as necessary to assess the engineering properties of a material. In this case, some of the error sources start to become more important; for example, accurate sample temperature measurement. The third type is required for more fundamental studies and, in this case, all of these error sources may be relevant and, therefore, should be considered.

7.1 Calibration Issues

The calibration of the various measurement devices on an instrument is obviously a prerequisite to the performance of accurate sorption measurements and it plays a part in some of the topics discussed in the following sections. In addition to the calibration of the temperature and pressure measuring devices, volumetric and gravimetric instruments require calibration of their reference volumes and of the microbalance, respectively. The former ensures that an accurate value is calculated for the number of moles of gas present in the system at a given hydrogen pressure and temperature; the latter that the empty balance (pan) reading, the empty or dry sample mass and the mass of the sample during uptake are measured accurately. Volume calibration for volumetric instrumentation is discussed further in Section 7.8. Keller and Staudt [40] show the variation of the measured volume of a calibration cylinder with gas type (helium, nitrogen and methane) and pressure, using a commercial gas pycnometer, demonstrating that care must be taken during volume calibration. The use of an accurate value for the volume is particularly important in the volumetric method because of the accumulative errors that can occur during the measurement procedure (see Section 7.15). In TPD, the calibration of the hydrogen signal is particularly important to the accuracy if the desorbed quantity is determined using a mass spectrometer [110,115,124].

7.2 Temperature Monitoring and Control

Temperature monitoring and control are clearly important in all temperature and pressure ranges in each technique. In general, in isothermal measurements the further the sample temperature is from ambient, or the chosen operating temperature of the rest of the apparatus, the greater the likelihood of problems with temperature gradients[23]. Therefore, adsorption measurements performed at low (liquid nitrogen) temperatures and high temperature absorption measurements performed on hydrides may be affected the most. However, a poorly thermostatted system will obviously cause problems regardless of the sample temperature, and a range of claimed temperature stabilities can be found in the literature. The IUPAC guidelines [27] suggest that, for low temperature nitrogen adsorption apparatus, volumes with 'appreciable' amounts of gas should be regulated to within ± 0.1°C but that the whole apparatus should be "maintained at reasonably constant temperature". This requirement, however, was not included in the subsequent BET Method standard [167], which simply states that "the various volumes of the apparatus and their temperatures should be taken into account". JIS H 7201-1991 [163] specifies ± 0.5 K for both the control of the thermostat temperature and the measurement of room temperature. Blackman et al [177] specify a stability of ± 0.1 °C and Gerard et al [50] state that the temperature must be regulated to within 0.05 K. However, regardless of the estimated uncertainty in the temperature, the important point is not how carefully a single sensor monitors a particular point in the apparatus but how well the measured temperature represents the uniformity of the temperature throughout the system.

The problem of 'cold spots', whereby part of the apparatus is at a lower temperature than the rest, thus leading to the false measurement of adsorption in the volumetric technique, was identified by the IUPAC guidelines [27]. Gravimetric measurements will not be affected as much because the assumption of isothermal conditions is not relied upon to calculate the total sorbed quantity. In the case of measurement at the critical temperature of an adsorbate then a cold spot could lead to bulk condensation. At the elevated temperatures ($> T_c$) at which hydrogen sorption is normally performed, bulk condensation will not occur but results will be affected nonetheless. The reverse effect (or 'hot spots') will also affect volumetric measurements.

This issue also includes strategies for dealing with the region of volumetric apparatus containing the temperature gradient. It also depends on the chosen dead volume calibration method (see Section 7.8) and is discussed, with regard to low temperature, low pressure adsorption measurement, by Rouquerol et al [26].

---

[23] The entire apparatus can be kept at one temperature [168]; however, this greatly restricts the operating temperature range.

7.3 Sample Temperature Measurement

In the volumetric technique a temperature sensor can be in direct contact with the sample during measurement, whereas in gravimetric measurements the sensor can only be in the vicinity of the sample [27]. This would suggest that sample temperature measurement is more accurate in the volumetric technique (assuming equivalent accuracies in the temperature measuring systems); although by not being in contact with the sample the sensor itself does not perturb the sample, which may in some cases be an advantage. However, providing that calibration is carried out carefully, the sample temperature should be determined to a reasonable accuracy in gravimetry. For example, Ma et al [102] pay particular attention to the accurate determination of the sample temperature for their gravimetrically-determined (non-hydrogen) TPD measurements. They state the location of the thermocouple and also confirm the correspondence of the sample and measured temperatures using complementary thermal decomposition and differential thermal analysis (DTA) measurements. The temperature calibration of microbalance samples, including the use of thermomagnetometry[24], is discussed in more depth by Brown [106]. The issue is, however, complicated by the presence of hydrogen itself, which has a high thermal conductivity. Going from high vacuum to above ambient pressures of any gas will greatly alter the heat transfer between the sample and the external walls of the microbalance vessel, but with hydrogen the effect is greater than with other common sorbate gases. With the exception of helium, which has a thermal conductivity of 0.1574 W m^{-1} K^{-1}, hydrogen's thermal conductivity (0.1971 W m^{-1} K^{-1}) is much greater than other adsorptives, such as nitrogen (0.0275 W m^{-1} K^{-1}), argon (0.0190 W m^{-1} K^{-1}) and carbon dioxide (0.0183 W m^{-1} K^{-1}) [179][25]. This effect will occur to a certain extent in volumetric measurements as well.

The BET Method standard [167], like JIS H 7201-1991 [163], does not specify a required uncertainty, but simply states that the sample temperature should be monitored. In TPD the measurement and control of the sample temperature is very important. Problems will be caused if there is insufficient heat transfer to the sample. The investigation of the effect of different sample temperature ramp rates on the data can help.

7.4 Thermal Effects from the Sample

Any sorption process will have an associated temperature change, either endo- or exothermic. In the case of hydrides[26], the exothermic effects of hydrogen absorption can be severe. This is a well-known issue with regard to kinetic sorption measurements on intermetallic hydrides [169,180] and several ways of reducing temperature excursions during quasi-isothermal experiments have been suggested [181,182]. In a recent article, Sandrock et al [69] report a 79 degree (428 to 507K) temperature excursion within one minute in a 100g $NaAlH_4$ bed upon hydrogen sorption. During isotherm determination there will not be such a large excursion, as the sorption process occurs in a stepwise fashion and the material is therefore not loaded in one aliquot. However, significant changes may still occur and it is important

---

[24] Using a ferromagnetic material of known Curie point.

[25] The figures quoted are for P = 101kPa and T = 273K.

[26] Specifically those being considered for hydrogen storage.

that this is monitored and that the sample is allowed to return to the required temperature after the application of each pressure step. Although the repeated heating and cooling of a hydride sample may lead to some changes in the measured isotherm through, for example, the completion of micro-hysteresis loops, it should not greatly affect the overall measured uptake, although this is material-dependent. However, in an investigation into the origins of the large-aliquot effect in $LaNi_5$, Gray et al [170] explain how temperature gradients within a hydride sample, caused by the heat of reaction, could lead to the apparent shift in the plateau pressure seen when samples are hydrogenated using different pressure step sizes in volumetric apparatus. In a subsequent paper, Kisi and Gray [171] observed the spatial inhomogeneities in the hydrogen content (α/β phase proportions) of a sample as a result of temperature gradients within a $LaNi_5$ hydride sample, which suggests that thermal effects from the sample in this case are very significant in the characterisation of the equilibrium properties.

In general, the heat of reaction will be dissipated more rapidly in volumetric apparatus, in which the sample is in contact with the sample cell walls, compared to a gravimetric system in which the sample is suspended in a pan in a relatively large volume. However, this should not actually affect the accuracy of a measurement, it is just important to allow a return to the original temperature before an actual isotherm point is determined. If this is not done an elevated sample temperature profile will be seen through the ‘isotherm’, providing the sample’s actual temperature is monitored accurately throughout the measurement.

7.5 The Approach to Equilibrium

In the same way as it is important to wait for thermal equilibrium to be re-established after each step in isotherm measurement, it is also important to make a measurement when the sample has reached sufficient equilibrium, in terms of hydrogen sorption. In microporous adsorbents the sorption takes the form of the diffusion of molecular hydrogen through the porous network until a form of equilibrium has been reached (so there is no significant concentration or pressure gradient through the sample). In hydrides, it may be any number of processes, including the diffusion of atomic hydrogen through a solid solution (α) or hydride (β) phase, or a phase transition, with associated nucleation and growth. In all cases, the sorption process can be monitored either by the pressure change, in the case of volumetric measurement, or the weight change, in the case of gravimetric measurement. The period over which this occurs can be vastly different for different materials, for a number of reasons, but also different through the course of an isotherm [86], and so this should be monitored carefully. Although the time-dependent data gives the most information in this respect, problems with non-equilibrium measurement can be diagnosed to a certain extent from the shape of the resultant isotherms. For example, if an absorption isotherm measurement is being performed on a hydride that shows a clear plateau region and sufficient time for equilibrium is not allowed, the plateau will be shortened, particularly at the higher hydrogen content end. If the isotherm is plotted as pressure against hydrogen content, the β phase section will also have a lower gradient than would be expected. The approach to equilibrium is easier to monitor gravimetrically than volumetrically, providing the gravimetric measurements are isobaric, as changes in or on the sample are measured directly. For example, Stonadge et al [76] presented the isobaric uptake behaviour of hydrogen in a Pd-Y alloy, and Reid and Thomas [183] measured the kinetic uptake of various adsorptives by a carbon molecular sieve. In both of these cases, the analysis of the kinetic uptake for a particular sorption step allowed confirmation that an appropriate level of equilibrium had been achieved during isotherm determination, although in the latter case some of the predicted equilibrium times were too long to be measured (> 180 days).

Rouquerol et al [26] discussed this issue with regard to adsorption equilibrium, stating that the confirmation of adsorption equilibrium is of crucial significance and suggesting a suitable approach. Keller and Staudt [40] refer to the confirmation of adsorption equilibrium to a sufficient degree as reaching *technical equilibrium*. It is important to note that, in the case of hydrogen, the time required for equilibrium to be achieved is likely to be longer for absorption than adsorption [88,93]. The various degrees of equilibrium possible in the plateau region of metal hydrides were discussed recently by Flanagan and Oates [184].

7.6 Sample Size Considerations

There are a number of ways in which the sample size can potentially affect the accuracy of a measurement. The most obvious case is that of a sample being too small for the lower detection limit (or sensitivity) of the instrument or technique. So, for example, in volumetric measurement a hydride sample being too small for a particular system volume (see Section 7.8). Poirier et al [62] and Lee et al [178] have recently presented both instrumentation and results on small samples; although Poirier et al [62] do not show any isotherms and the Lee et al [178] data on activated carbon show a significant sample size dependence, with the smallest (6 mg) sample showing a greater wt.% uptake than the larger samples (39 and 251 mg). Interestingly, although it is not commented on and isotherms are not shown, Poirier et al's [62] volumetrically determined Pd data (in wt.% or H/M) show an approximate correlation with sample size whereas their gravimetric data does not. This work was prompted by the special case of carbon nanotubes, which can only be synthesized in small quantities. Otherwise, sample size selection for microporous adsorbents that have less of a size restriction (such as MOFs), or for hydrides, should be made, where possible, on the basis of the selection that will give the highest accuracy for the measurement [53].

Rouquerol et al [26] discuss sample mass selection for porous materials, in general, suggesting that sample mass choice be based on the specific surface area (SSA). They suggest that the most reliable results will be obtained with a total area of 20 to 50 m^2. However, for samples with an SSA of greater than 500 $m^2\ g^{-1}$ care needs to be taken not to reduce the sample mass too much and to weigh the sample with an accuracy that is consistent with the adsorption measurement accuracy. Therefore, masses of less than 50 mg should be avoided. This would suggest that, in the case of microporous adsorbents, sample masses should be kept down in the region of 50 mg because the measured SSA will normally be > 500 $m^2\ g^{-1}$ for these materials. However, this refers to the measurement of the adsorption of gases other than hydrogen at sub-ambient pressure. Furthermore, for microporous materials, the BET method is known to be unreliable [167] and the use of the concept of SSA is questionable; although the assumption of Langmuir-type monolayer coverage behaviour (for nitrogen at 77 K) appears to give reasonable values for an apparent surface area for MOFs [159][27]. These and related issues are discussed by Rouquerol et al [26]. However, the important point is to correlate the sample size choice with both the expected hydrogen uptake and the accuracy of the instrument, and, if there any doubts, to investigate the effect of the sample size on the measured uptake. For hydrides, JIS H 7201-1991 [163] suggests a sample mass of 0.1 to 100 g, which allows sample sizes that could presumably result in large temperature gradients (see Section 7.4). In gravimetric measurements the low mass of hydrogen means that sample sizes should not be reduced too far. However, this will depend on the sensitivity and long term stability of the balance, and the expected hydrogen uptake.

7.7 Gas Purity

Gas purity is important, including both the original supplier's purity and the filtration applied *in-situ*. Filtration is particularly important if the gas bottle is not connected directly to an instrument, as gas delivery lines can introduce significant levels of contamination. The effects of gaseous impurities on the hydrogen sorption process depend on both the material and the impurity type, but they include preferential adsorption and the poisoning or passivation of the surface [142,187-193]. The IUPAC guidelines [27] suggest that for BET measurement, the nitrogen purity should be > 99.9 %, although in the subsequent standard [167] this is increased to > 99.99 %. However, in hydrogen sorption measurement, the hydrogen purity should be higher than both of these figures (> 99.999 %). Depending on the experimental requirements, hydrogen can also be supplied directly from a metal hydride bed to provide even higher purity [194]. Any severe problems with gas purity should become apparent during initial test measurements with relatively well understood materials[28]. Additionally, for microporous materials, the gravimetric technique allows for the analysis of the kinetic behaviour of gas uptake, which varies greatly with the gas type [183,196]; and so, in the same way as the isotherm shape can give information about the nature of the adsorption, the form of the kinetics at each sorption step (see Section 7.5) can be used to help determine the likelihood of the experimental results being affected by the sorption of contaminants[29]. This was recently explained by Thomas in a review of hydrogen adsorption and storage on porous materials [11]. In the article gas purity is identified as a crucial accuracy issue in the measurement of adsorption and the importance of confirming the complete reversibility of the measured hydrogen

---

[27] Recent modelling work has concluded that the BET method is applicable to MOFs [185,186], by comparing geometrically-calculated surface areas with those determined from the BET analysis of nitrogen adsorption isotherms simulated using the Grand Canonical Monte Carlo (GCMC) method. Düren et al [186] argue, however, that it is important to use the accessible surface area rather than the Connolly surface area, the definition that is commonly used in molecular simulation. This is not directly relevant to the question of sample size choice in hydrogen adsorption measurement, as the minimum sample size would appear to be limited by the particular measurement system characteristics and the accuracy with which the sample mass can be determined; however, it is of crucial importance in the comparison of model isotherm data with experiment, any attempted estimate of the total adsorbed quantity from experimental data (see Appendix A) and in the definition of the sample density.

[28] Pd or $LaNi_5$ for higher temperature absorption measurements, for example, or a zeolite for low temperature adsorption measurements. High surface area reference materials are available, although they are mesoporous and of relatively low SSA ($\approx 250\ m^2\ g^{-1}$) [195]. A Ti alloy standard (SRM 2453) is also available from NIST.

[29] Hydrogen appears to exhibit particularly rapid kinetics in comparison to gases of larger molecular size [88,93].

uptake is emphasized. The consequences of impurity gettering by a hydride sample in a gravimetric system were discussed by Gray et al [78].

7.8 System Volume to Sample Size Ratio

The system volume to sample mass, or sample size, ratio is an important consideration in volumetric instruments. This was identified as one of the important factors in kinetic measurements on intermetallic hydrides by Wang and Suda [169]. It affects both system design and sample size choice. There are a number of inter-related factors, which depend very much on what is required of the instrument. If measurements are to be performed on an existing instrument then this may just become a case of sample size selection (see Section 7.6); otherwise it is a case of optimizing the system volume for a required sample size. The system volume must be small enough that the required quantity of hydrogen that is sorbed results in initial and final hydrogen pressures significantly far apart compared to the uncertainty in the pressure measurement. This may require either variable reference volumes or the careful choice of sample size, based on knowledge of the sorption properties of the material, or both. However, it may also be necessary to ensure that the initial pressure is not too high, in the case of materials that may undergo a phase transition during hydrogenation, in order to reduce material-related problems like the large-aliquot effect [170]. The system volume should also not be so low that the expansion of the material upon hydrogen absorption, and through the course of a full isotherm, results in a significant reduction of the system dead volume. In dense host materials with high volumetric hydrogen capacity this should not cause a problem.

Wang and Suda [169] defined the volume-mass relationship for the design of an experimental set-up,

$$V_{sys} \geq \frac{(C_f - C_i)N_a RT}{2M(P_i - P_f)} m \geq K_\alpha m \tag{2}$$

where V_{sys} = the system volume, m = the sample mass, C_i = the initial hydrogen concentration (H/M) at the initial pressure P_i in MPa, C_f = the hydrogen concentration (H/M) in the alloy after reaching equilibrium at pressure P_f in MPa, N_a = the number of atoms per formula unit (N_a = 6 for AB_5, N_a = 2 for AB), R = the universal gas constant, T = the temperature, and M = the molecular weight of the alloy. K_α is then defined as a coefficient for each alloy, with units of ml g^{-1}. Although this was defined for a single kinetic measurement, it should be applicable to a single isotherm step, where C_i is the hydrogen concentration at one point and C_f is the concentration at the next.

In the case of adsorption, the system volume includes the pore volume and (interparticle) void space. The dead space volume calibration is covered briefly in the IUPAC guidelines [27] and in more depth by Rouquerol et al [26]. Using helium to determine the dead space involves the, perhaps problematic, assumptions that helium does not adsorb at the temperature of the measurement [47-49] and that helium can 'see' the same volume as the hydrogen. According to Neimark and Ravikovitch [47] the former assumption leads to an overestimation of the pore volume of microporous materials and an underestimation of the measured excess adsorption isotherms.

However, these issues do not appear to have been widely discussed or investigated in recent adsorptive hydrogen storage literature. So, in terms of the dead space volume to sample size ratio, in the case of adsorptive storage, the dead space volume should not be so large that the expected excess adsorption cannot be detected by the pressure drop. However, if the dead volume is too low, the measurement may become too dependent on the dead space volume definition, the definition of the skeleton (or chemical) density of the sorbent or the measurement of the degassed sample mass (see the next section). If there are significant errors arising from the assumption of helium being non-adsorbing, the greater the proportion of the dead space that can be attributed to (inaccurately determined) micropore volume then the greater the effect of that error. Neimark and Ravikovitch [47] suggest that "an appreciable effect" of helium adsorption at 77K occurs in carbon micropores narrower than approximately 10Å. Malbrunot et al [48] performed helium density measurements volumetrically on four zeolites, one porous and one non-porous carbon, and a silica gel and concluded that the helium density determination should be carried out at elevated temperatures of up to 400 °C to avoid helium adsorption errors.

In a recent study, Blach and Gray [53] examine the issue of volumetric system design, with regard to low density host materials, noting that the effect of a change in sample density, ρ, on the calculated hydrogen uptake depends on ρ^{-2}. In the article the authors use what Rouquerol et al [26] refer to as the *indirect route* for dead volume determination, which avoids the issue of the assumption of helium being non-adsorbing but, as the authors demonstrate, leads to problems relating to the estimated density of the sample. They show that a poorly designed system can give errors of up to 100% in the calculated sorbed quantity, and they introduce a figure of merit design parameter,

$$\eta = \frac{s_k}{\delta p} \tag{3}$$

where s_k indicates the sensitivity of the system to changes in the amount of sorbed hydrogen and δp is the useable resolution of the pressure measuring device. They propose that η should be ≥ 100 to minimise the errors. In support of their proposal they present hydrogen uptake data measured on three different volumetric (manometric) instruments with three low density material types: carbon nanotubes, potassium-intercalated graphite and lithium nitride. In addition, they also express doubts about the *direct route* [26] of dead volume determination, and discuss the importance of the ratio of reference cell to sample cell volumes.

7.9 Sample Degassing

Before any sorption experiment a material and the apparatus must be degassed[30] to a certain extent. In the case of adsorbents this process is crucial in preparing the sample's surface for adsorption. In general, it is necessary to begin an adsorption measurement with the surface in a state appropriate for the application for which the material is being considered [26]. For hydrogen adsorption a 'clean' surface is required, although there may be exceptions, depending on the definition of a 'clean' surface. Generally, however, any environmental adsorbates that could react with hydrogen or be desorbed in the temperature range of interest must be removed. This issue is covered by the IUPAC guidelines [27], and two approximate thresholds for degassing pressures are identified. Firstly, around 10 mPa (10^{-4} mbar) is suggested as a satisfactory residual pressure for degassing a sample for the purpose of a surface area or porosity determination measurement; this is in the high vacuum range [198]. Secondly, it suggests that an ultra high vacuum (UHV) pressure of less than 1 μPa (10^{-8} mbar) may lead to changes in surface composition, the formation of surface defects or irreversible changes in texture. In a later section, it also refers to a basic UHV pressure of 100 μPa (10^{-6} mbar), which is closer than 1μPa to an achievable level in sorption apparatus constructed from UHV components. However, the important point is that even the highest of these pressures requires a pump suitable for UHV systems, which typically means a turbomolecular pump; see, for example, Thomas [11]. The BET Method standard [167] suggests 1 Pa as "usually sufficient" for degassing, but also mentions the requirement of a vacuum "better than 10^{-2} Pa" for the zero point of a gravimetrically-determined isotherm. The standard also includes instructions for monitoring the degassing process.

During the degassing procedure it is the pressure above the sample that is important and this often cannot be measured directly. The geometry of the sorption apparatus will have a significant effect on the achievable vacuum over the sample and the rate at which it will be achieved, due to the conductance of the tubing. A system constructed of UHV components, large bore tubing and having a relatively direct path from the vacuum pump to the sample will achieve a different level of vacuum in the sample cell than a system constructed of narrow tubing with a more complex route (including, for example, several valves) from the pump to the sample cell. As an example, from recent hydride work, Vajo et al [68] replaced their sample cell with an ionization gauge to determine the quality of the vacuum achievable on their sample and found that a base pressure at their pump of $< 1.3 \times 10^{-6}$ Pa resulted in a pressure of 1.3×10^{-4} Pa near their sample after pumping overnight. In this case the sample cell was separated by approximately 1 m of 0.953 cm outside diameter tubing, several valves and a 2 μm filter gasket. With a different length of tubing, different geometry, different filtration, and so on, this value would be different and the length of time taken to achieve an equivalent vacuum would be different. In addition, there are

---

[30] In vacuum science, *outgassing* is defined as the evolution of gas from a solid or liquid in a vacuum, *degassing* as the deliberate removal of gas from a solid or liquid in vacuum as a result of the impact of molecules, electrons, ions, or photons; or by heating and *desorption* as the release of adsorbed atoms and/or molecules, either neutral or ionized, from the surface of a solid or liquid as a result of the impact of molecules, electrons, ions, and photons; or by thermal energy at the temperature of the material [197]. Using these definitions, *degassing* is the most appropriate term in this case, because we are interested in deliberately removing gas, or liquid, either by heating in a vacuum or by bombarding the surface with inert gas molecules.

further material-related considerations, with the degassing temperature being another essential factor in the degassing process. This will depend on both the adsorbate species to be removed and the thermal stability of the material. In the case of carbon materials, for example, the results of degassing the sample at different temperatures can be significantly different [132] and can have implications for the material's subsequent readsorption of environmental adsorbates upon exposure to air. The sample's subsequent storage conditions will then have an effect on the material's properties (see the following section).

An important related issue is the accurate determination of the dry sample mass. In gravimetry the sample mass can be monitored during the degassing procedure. Once the mass has stabilized under conditions suitable for the particular material, the measured value can be used as the dry sample mass[31]. In the volumetric technique this is not possible and an alternative method of determining the degassed sample mass must be used. The significance of this as a source of error is dependent on the type of material; for example, if an adsorbent is hydrophilic (for example, a zeolite) there may be a larger wt.% uptake of water to be removed than for a hydrophobic adsorbent (for example, a carbon). Another example is the removal of solvent from the pores of a MOF, which could also contribute to a larger reduction in sample mass during the degassing process.

For hydrides that can be exposed to air, degassing is not as crucial as for porous adsorbents but it is still an important part of the activation procedure. If an unactivated sample is not degassed sufficiently [169] the environmental adsorbates are likely to inhibit the initial surface activation process [13].

7.10 Sample Pretreatment and History

A sample's history, including periods of storage, can have a significant effect on its sorption properties and so it is important that this is known and recorded, particularly if the results from two samples are to be compared. This was identified as one of the key problems in (volumetric) kinetic measurements on intermetallic hydrides by Wang and Suda [169]. In this case, the sample's history includes periods of exposure to air, which are shown to greatly affect the initial hydrogenation reaction, and the number of hydrogenation/dehydrogenation cycles. Robens et al [199] noted, with regard to high surface area candidate reference materials, that the surface could be substantially affected during storage and sample preparation. Therefore, when testing reproducibility, results from microporous materials that have been stored differently should only be compared, for the purpose of assessing measurement accuracy, if the sample degassing procedure can be guaranteed to return the sample's surface to its original state. The sensitivity of a microporous carbon to its storage conditions was shown by Avraham et al [132]. The importance of a complete knowledge of a sample's thermal history, in the context of intermetallics, was discussed in detail by Buckley et al [172]. They concluded that the sensitivity of the physical properties of $LaNi_5$-H with regard to the sample's thermal history is such that the detailed thermal history of the sample should be quoted when data are published.

---

[31] Although the mass measured at vacuum can be affected by thermomolecular flow effect disturbances of the balance (see Section 7.13), depending on the presence and the level of temperature gradients in the system, and so care needs to be taken.

7.11 Pressure Measurement

Pressure measurement [200] is obviously important in both the volumetric and gravimetric techniques. In the volumetric method it is used to calculate the sorbed quantity and therefore must be determined to sufficient accuracy; however, the accurate determination of the pressure is also crucial for gravimetric techniques. In temperature-programmed techniques its importance depends on how the desorbed hydrogen is being measured. JIS H 7201-1991 [163], referring to the volumetric method, states that the pressure should be measured using an instrument "with precision of three or more significant digits at the maximum service pressure". The IUPAC guidelines [27] suggest that for nitrogen BET the pressure should be measured to within ± 10 Pa, which applies to both volumetric and gravimetric methods, although in the sub-ambient pressure range. As with temperature measurement, this requirement is omitted from the subsequent standard. The choice of pressure measuring device for volumetric measurements must be so that the uncertainty in the pressure measurement is not significant compared to the expected drop in pressure upon hydrogen absorption, or vice versa, for the chosen sample size (see Section 7.8). If measurements are to be made over a wide range of pressures then this may require different devices covering different pressure ranges, in addition to the vacuum gauge or gauges used to monitor the pump system.

7.12 The Compressibility of Hydrogen

An issue important in high pressure measurement is the accurate representation of the compressibility of hydrogen. If hydrogen is treated as an ideal gas during the volumetric determination of hydrogen uptake at above ambient pressure, significant errors will be introduced to the calculated sorbed quantity. The pressure-density relationship for hydrogen must therefore be represented by an alternative equation of state (EOS). This is a well-known correction[32] that must be applied to experimental isotherm data but the actual choice of EOS, over the entire temperature and pressure regime, does not appear to be quite so clear-cut. JIS H 7201-1991 [163] simply states that "the compressibility shall be corrected".

Zhou and Zhou [174] identified the Soave-Redlich-Kwong (SRK) and Benedict-Webb-Rubin (BWR) equations as suitable candidates for use with hydrogen in the case of adsorption measurement. The former is a cubic EOS in which the required parameters are the critical temperature, pressure and the eccentric factor; the latter is a higher order expansion of the virial EOS, with eight empirically determined parameters. Kiyobayashi and co-workers [61] chose a modified version of the BWR EOS, known as the 32-term modified BWR EOS, which, along with the SRK, is the same as that chosen by Zhang et al [173]. However, Kiyobayashi et al [61] and Zhang et al [173] perform measurements only at near ambient temperatures, and Zhou and Zhou [174] use an eight parameter form of the BWR equation with parameters that are valid only in the range 0 - 150 °C (273 - 423 K). Therefore, in this work, the BWR EOS in its 8-term and 32-term modified form has only been examined or tested at near ambient temperatures. The 32-term modified BWR EOS can, however, describe

---

[32] In his introduction, for example, Fukai [14] mentions a 6% volume deviation from an ideal gas at 10MPa and 300K.

the behaviour of hydrogen at temperatures down to around 14 K [201]. Zhou et al [66], in their recent study of high pressure hydrogen and methane adsorption in MOF5 and ZIF8, compare the modified BWR with the van der Waals (VDW) EOS and the ideal gas law. They conclude that the modified BWR EOS[33] describes the behaviour of hydrogen, in the low temperature and high pressure range, the most accurately. Their plot of the false hydrogen adsorption at 77 K calculated using the VDW EOS, which does not provide an adequately accurate description of the real gas behaviour at this temperature, shows the significant errors that can be introduced through a poor choice of EOS.

The most accurate EOS for hydrogen at higher pressures and temperatures is considered [203] to be that of Hemmes et al [204], although this was not used or examined by Zhou and Zhou [174], Kiyobayashi et al [61] or Zhang et al [173] for their near ambient and lower temperature work. Within the pressure and temperature range for which it is intended ($P \leq 1$ Mbar and $100 \text{ K} \leq T \leq 1000$ K), the Hemmes et al EOS [204] reproduces experimental data to within 0.5 %, although in our region of interest the data are reproduced to within 0.1 %. However, the region below 100 K, as examined by Zhou and Zhou [174] using the SRK EOS and by Zhou et al [66] using the VDW and modified BWR EOS, is not covered and it is not clear which of these would be more suitable. Another EOS was presented by Tkacz and Litwiniuk [205] but this has not been widely tested for use in the volumetric determination of hydrogen uptake. In addition, Lemmon et al [201] recently presented an EOS for hydrogen that accurately describes its behaviour in the temperature range 220 - 400 K and at pressures up to 45 MPa. If measurements are being performed with deuterium the EOS presented by McLennan and Gray [203] would appear to be the most accurate, although this does not cover the low temperature regime.

It is worth noting that an accurate description of the compressibility of hydrogen is also required for the gravimetric technique at higher pressures, as the buoyancy effect corrections (see Section 7.14) require knowledge of the gas density as a function of pressure. However, the effects of an inaccurate description will not be as significant as with volumetric determination in which the introduced errors can accumulate greatly through the measurement of an isotherm, as demonstrated by McLennan and Gray [203] with deuterium absorption data for Pd (see also the adsorption data of Zhou et al [66]).

7.13 Thermal Transpiration (Thermomolecular Flow) Effects

At low pressures, in both volumetric and gravimetric measurement, another source of error is the occurrence of thermal transpiration, also known as thermomolecular flow, whereby a thermal gradient along a tube of a diameter close to, or below, the mean free path of the gas molecule will result in a pressure gradient along the length of that tube. In practical terms, this can occur when measuring the pressure of a system, or the pressure of a sample cell or calibrated volume, that is at a temperature different from that of the pressure measuring device. Wallbank and McQuillan [206] applied thermal transpiration corrections to Ti/H data at low pressures, showing that the effects can be significant, and the issue is also covered by Rouquerol et al [26] in the

---

[33] As used by REFPROP, the NIST Reference Fluid Thermodynamic and Transport Properties Database software [202].

context of adsorption measurement. In both high temperature (absorption) and lower temperature (adsorption) measurements, errors as large as 100 % can be introduced to the pressure measurement [26,206].

The likelihood of the occurrence of this effect can be assessed by considering the Knudsen number, *Kn*, of the system ($Kn = \lambda / L$), where λ is the mean free path of a hydrogen molecule and *L*, the length scale, which, in this case, corresponds to the tube diameter. Figure 4 and Figure 5 can be used to assess this for hydrogen. Figure 4 plots the mean free path against pressure for a number of temperatures, for most of the temperature and pressure regime of interest for storage applications. Figure 5 plots the characteristic length scale, *L*, against λ for three different Knudsen numbers (0.01, 0.1 and 1.0) representing approximate thresholds. Typical sorption apparatus can contain components (including tubing and valves) on length scales from sub-mm to a few cms. The threshold for the free molecule regime ($Kn > 1.0$) is reached when the mean free path exceeds these dimensions. It can be seen in Figure 4 that the lower limit (sub-mm) can be exceeded at pressures as high as 10^2 to 10^3 Pa, depending on the temperature. This indicates that thermal transpiration effects could easily be significant during low pressure hydrogen sorption measurements. For their experiments, Wallbank and McQuillan [206] suggest corrections are necessary below 15 Pa. Wilson et al [31], in a recent low temperature (20 - 100 K) adsorption study, corrected all pressure measurements below 2 torr (0.267 kPa).

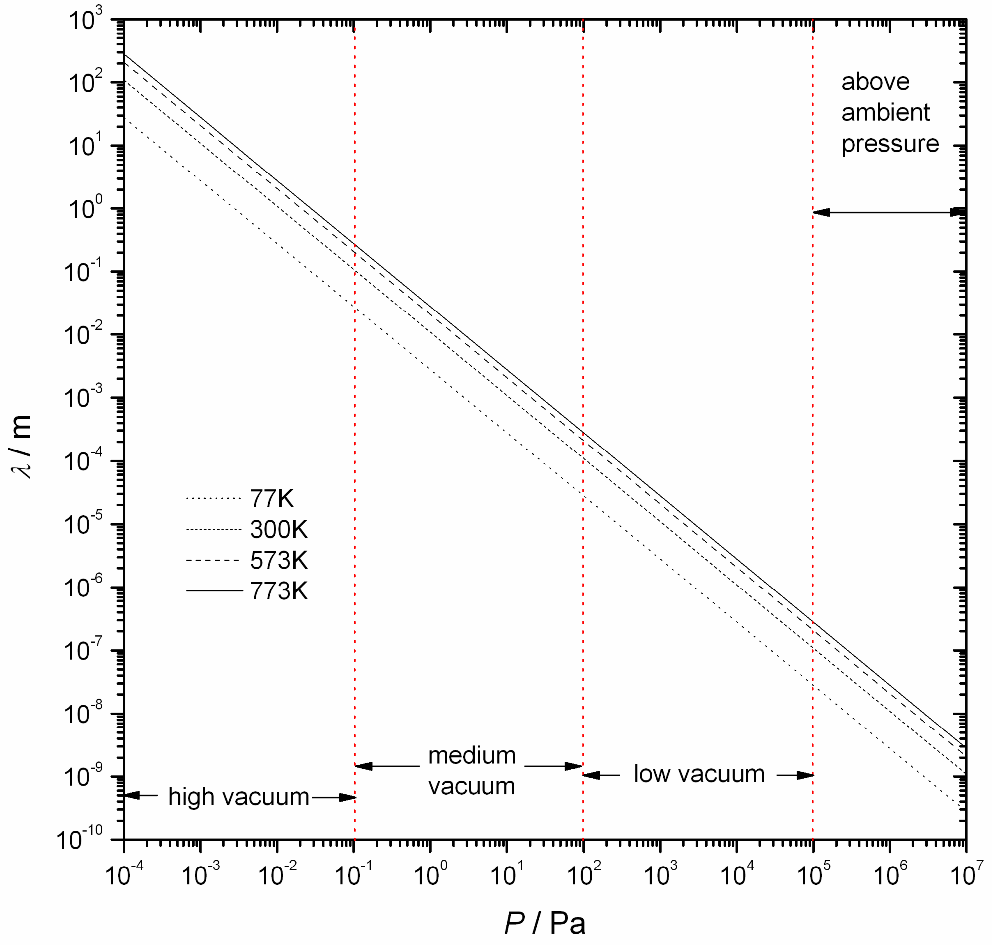


Figure 4. A plot of mean free path, λ, for hydrogen at a range of temperatures, against pressure, P, in the typical operating pressure range of hydrogen sorption apparatus.

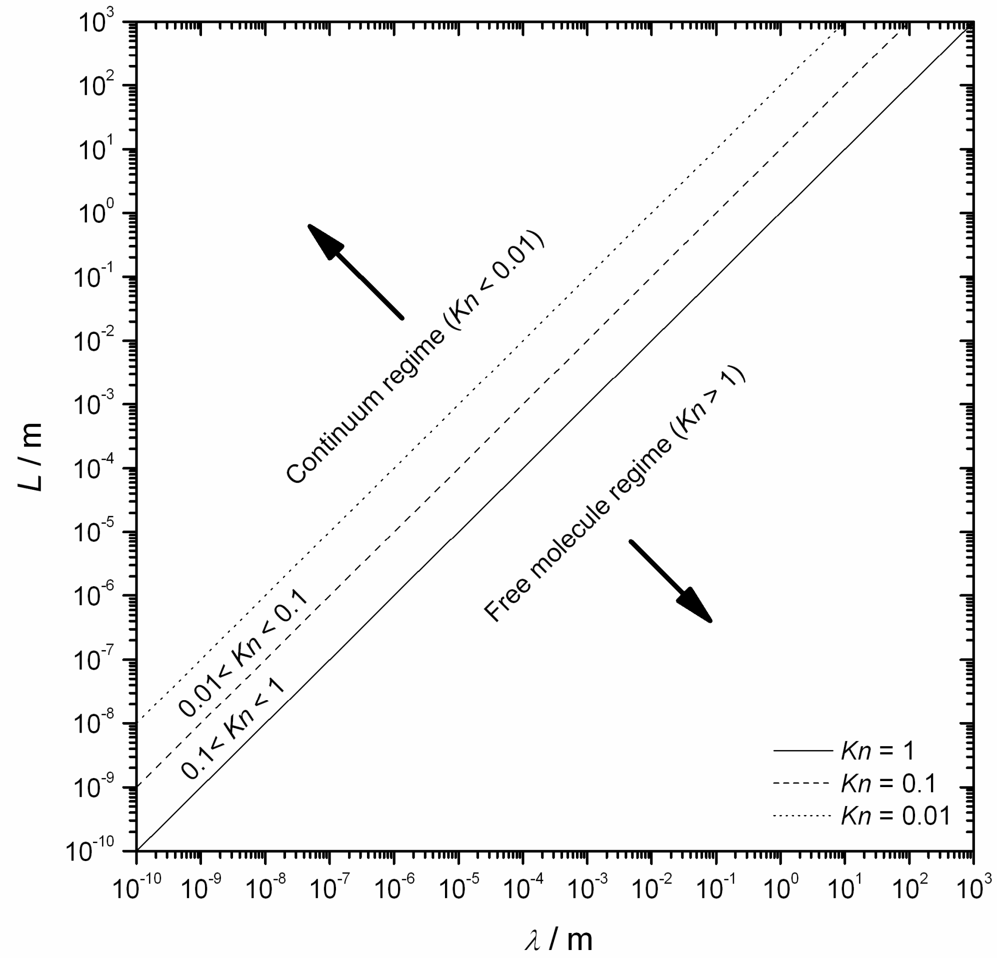


Figure 5. A plot of the characteristic length scale, L, of a system against mean free path, λ, for different Knudsen numbers, indicating the free molecule and continuum regimes, with the transitional region (approximately $0.01 < Kn < 1$) in between.

For $Kn >> 1$, using the tube diameter as the characteristic length scale, the correction necessary for thermal transpiration effects is given by,

$$\frac{P_t}{P_m} = \left(\frac{T_t}{T_m}\right)^{\frac{1}{2}} \tag{4}$$

where P_t = the true equilibrium pressure, at the sample temperature T_t, and P_m = the measured hydrogen pressure, at temperature T_m. As Kn approaches one, the thermal transpiration effect decreases with increasing pressure, becoming zero once the pressure is above a certain threshold (once the system has entered the continuum regime). In the transition region, the pressure dependence must be accounted for and a number of approaches have been taken [26,206-208]. Knudsen's original derivation gave,

$$\frac{P_t}{P_m} = \left(\frac{T_t}{T_m}\right)^{\frac{\chi}{2}} \tag{5}$$

with

$$\chi = \left(1 + \frac{d}{\lambda}\right)^{-1} \tag{6}$$

where d = the tube diameter. However, Wallbank and McQuillan [206] represented χ in terms of the pressure and used the following empirical expression,

$$\chi = \left[1 + (P_m/P_0)^{1/2}\right]\exp\left[-(P_m/P_0)^{1/2}\right] \tag{7}$$

with P_0 = 3.4 Pa in their case. They demonstrate the correction with experimental data measured using significantly different tube diameters (3.5 and 18 mm).

Other empirical pressure corrections that are commonly quoted [31,32,209-212] include those due to Liang [207] and the later, modified version of Takaishi and Sensui [208].

Another consequence of thermomolecular flow is the disturbance of the microbalance during gravimetric measurements at low pressures. The disturbance effects, which occur in the presence of a temperature gradient across both the sample and the microbalance hangdown, are complicated and depend on a number of factors, including the geometry of the experimental set-up, the density and geometry of the sample, the hangdown, and the gas type [213-216].

7.14 Buoyancy Effect Corrections

The buoyancy effect corrections that are necessary for gravimetric data are often quoted as a significant source of error. They are the analogue of the dead space volume corrections in the volumetric technique, which account for the presence of the sample itself in the sample chamber. In the gravimetric case, the buoyancy corrections must also take account of the presence of the balance pan and hangdown in the balance chamber. Each of these components displace the hydrogen, following

Archimedes' Principle, by a volume dependent on their volume and the density of the hydrogen at the measurement temperature and pressure. The IUPAC guidelines [27] express the apparent change in weight upon sorption, Δw, as,

$$\Delta w = w - w_0 = \left[n_a - \frac{V_s}{v_g} \right] M \tag{8}$$

where w = the apparent weight after sorption, w_0 = the sample weight in vacuum, n_a = the apparent adsorption (the Gibbs excess), V_s = the volume occupied by the sample, v_g = the molar volume of the adsorptive (in our case hydrogen), and M = the molar mass of the adsorptive. Therefore,

$$n_a = \frac{\Delta w}{M} + \frac{V_s}{v_g} \tag{9}$$

The second term on the right hand side is the buoyancy correction. In gravimetry, the displacement of the gas manifests itself as an upward force on the balance, which can be expressed as a summation of the masses and densities of each component and the density of the gas at the relevant temperature and pressure (see Section 7.12). However, the implementation of the buoyancy effect corrections depends on the balance and the experimental configuration [40].

Although the volume of gas displaced will not increase appreciably[34] with increasing pressure and temperature, the buoyancy corrections will increase due to the increasing density of the gas, and so the corrections become of increasing significance at higher pressures. For an ideal gas the upward force will increase linearly with pressure; however, as soon as compressibility effects for a real gas become significant, deviation from linearity will occur. There is also a significant dependence on the sample density, with lower density samples requiring larger buoyancy effect corrections.

7.15 Accumulative Errors

The accumulative errors inherent in the volumetric measurement procedure are another frequently quoted error source. They occur when performing a measurement with more than one isotherm point. Any error introduced to the determination of the quantity of gas in a single aliquot, from any number of sources, including the pressure measurement, temperature measurement/gradient considerations, an inaccurate description of the hydrogen compressibility at higher pressures, leaks and the volume calibration, will accumulate through the measurement of a single isotherm. This is in contrast to the gravimetric technique in which the original sample mass reading is used as the reference point for each isotherm point, or the hydrogen uptake at a particular pressure.

---

[34] The change in sample density or volume, due to hydrogen sorption (for example, lattice expansion in hydrides), will depend on the material type.

7.16 Leaks

Practically, leaks can be a problem in volumetric measurement. The main issue is probably leakage through the valves of a system. If there is any significant leakage between the volumes in a system then the accumulative errors will be greatly increased. However, if an instrument is tested and operated manually these should be apparent during initial leak testing; if it is automated then the presence of significant leakage should be apparent from the shapes of measured isotherms on relatively well-understood materials, in a similar way to problems with non-equilibrium conditions (see Section 7.5), or from the performance of empty sample cell runs. In system design, the risk should be minimized by the use of high specification components and valves, and by limiting the chance of the sample (if in powder form) contaminating the system, using adequate filtration and by securing the sample sufficiently.

Leak testing of pressure equipment is commonly performed with helium, prior to the performance of measurements using hydrogen[35]. The fluid dynamics of gas leakage through small orifices, and hence the behaviour of different gases in similar situations, is not trivial. The behaviour of a gas depends on a number of factors but an indication of its behaviour in particular situations can be gleaned from the system's Knudsen number, as with thermal transpiration. Figure 5 shows a plot of the characteristic length scale of a system against mean free path for different Knudsen numbers, indicating the free molecule and continuum regimes, with the transitional region (approximately $0.01 < Kn < 1$) in between. It can be seen that at higher pressures and temperatures, the mean free path of hydrogen is such that the continuum regime begins at length scales of the order of microns. Lee et al [219] recently performed an experimental study on helium and hydrogen leak rates through small orifices. In addition, Schefer et al [137] recently examined the issue and present equations for different flow regimes (sonic, sub-sonic, turbulent, laminar, and so forth), as well as examining the permeation rates of hydrogen through different metals, which is relevant for the diffusion of hydrogen through the walls of instrument vessels. The permeation rates of hydrogen through 403 and 316L stainless steels are shown to be different by orders of magnitude.

In the continuum regime ($Kn < 0.01$), if there is choked (sonic) flow through an orifice (the leak source) with a short leak path, the mass flow rate is given by [219],

$$\dot{m} = DC\left(\frac{A_{orifice}P}{\sqrt{T}}\right)f(\gamma, R) \tag{10}$$

where DC is a discharge coefficient, $A_{orifice}$ is the cross-sectional area of the source, P is the vessel pressure, T the temperature and $f(\gamma,R)$ is dependent on the gas and is given by,

$$f(\gamma, R_m) = \left(\frac{\gamma}{R_m}\right)^{1/2}\left[\frac{2}{(\gamma+1)}\right]^{(\gamma+1)/2(\gamma-1)} \tag{11}$$

---

[35] Bley [217] covers the leak testing of vacuum equipment and the standard BS EN 1779:1999 [218] covers the non-destructive leak testing of pressure and vacuum equipment.

where $\gamma = \frac{c_p}{c_v}$, the ratio of the specific heat capacities of the gas at constant pressure, c_p, and constant volume, c_v, and R_m is the universal gas constant divided by the molecular mass. There is a slight pressure and temperature dependence for R_m and γ, but for our purposes they are not significant. For hydrogen, $R_m = 4.124$ kJ kg^{-1} K^{-1} and $\gamma = 1.41$ and for helium, $R_m = 2.077$ kJ kg^{-1} K^{-1} and $\gamma = 1.66$. If we assume that, for a single leak source, the discharge coefficients are the same for the two gases, and that there is choked flow, at a given temperature and pressure helium will leak more rapidly than hydrogen by nearly 50%. So, in this regime, if leak tests are performed with helium, any significant potential hydrogen leaks will be identified. However, this assumes that the system is in the continuum regime (see Figure 5).

8 CONCLUSION

In this report, the main techniques used for the gas phase characterisation of the equilibrium hydrogen sorption properties of potential hydrogen storage materials have been introduced and the practical considerations involved in the choice of sorption instrument discussed. The topic of measurement accuracy in the context of recent hydrogen storage material research, including the controversy over the storage properties of carbon nanostructures, has been covered, and recent work in the literature, including guidelines and standards on sorption measurement, has been reviewed. The potential sources of error in hydrogen sorption measurement and other experimental considerations have been discussed and categorised, with reference to the scientific literature.

The various sources of error have been separated into the following categories:

1) Calibration issues
2) Temperature monitoring and control
3) Sample temperature measurement
4) Thermal effects from the sample
5) The approach to equilibrium
6) Sample size considerations
7) Gas purity
8) System volume to sample size ratio
9) Sample degassing
10) Sample pretreatment and history
11) Pressure measurement
12) The compressibility of hydrogen
13) Thermal transpiration (thermomolecular flow) effects
14) Buoyancy effect corrections
15) Accumulative errors
16) Leaks

The significance of each issue has also been discussed, and a summary is presented in tabular form in the Appendix.

The recent controversy over the storage properties of nanostructured carbon has demonstrated how easily mistakes can be made during the experimental determination of hydrogen uptake. The measurement of hydrogen sorption is technically demanding for a number of the reasons already discussed and listed above. Reports of experimental hydrogen sorption measurement do not always provide sufficient experimental information to determine their validity [2,11]. However, it is likely that in some of the cases in which large hydrogen uptakes have been erroneously reported one or more of the error sources listed above played a significant role. Although some of the error sources, including the thermal effects from the sample and thermal transpiration effects, are unlikely to cause large errors in overall measured uptake, others, such as the presence of gaseous impurities, system leaks and inadequate sample degassing, could potentially lead to considerable inaccuracy in the measured hydrogen content of a material.

A significant amount of work has already been carried out on measurement accuracy-related issues, including the use of complementary techniques not discussed here, but there are still areas that have not yet been investigated thoroughly. As the search for new potential storage media continues, including novel solutions not mentioned in this report, it is important that hydrogen sorption measurement accuracy is better understood to ensure that further mistakes do not occur. Although the range of materials on which measurements are being performed is wide, there are many aspects of the measurement techniques and procedures that are common to all, or at least common to particular groups of materials, and it should be possible to clarify the effects of some of these through further experimental work, and inter-laboratory testing. Any further research that may lead to a clearer understanding of the effects of the various error sources would, in the author's opinion, be valuable and could also contribute to the possible development of hydrogen-specific sorption measurement standards. In addition to this, accurate gas phase hydrogen uptake measurement is crucial in gaining a greater understanding of the hydrogen sorption process, which is of significant importance in the development of new storage media, and so further work in this area would also aid the search for new hydrogen storage materials.

9 ACKNOWLEDGEMENTS

The author would like to thank M. Mercer, M. J. Benham, A. Walton, D. K. Ross, J. C. Davies and P. Moretto for useful discussions on various aspects of this work, and A. Feyel, A. Podias and E. Tzimas for their help with regard to hydrogen compressibility and leakage. In addition, I would like to express my appreciation to P. Moretto for his help during the completion of this report, and for providing valuable feedback, at various stages, on both the final draft and the earlier work on which the report is based. Partial funding by the European Commission DG Research (contract SES6-2006-518271/ NESSHY) is also gratefully acknowledged.

10 APPENDIX A: THE DEFINITION OF ADSORPTION CAPACITY

10.1 Introduction

The measured quantity in a volumetric or gravimetric hydrogen adsorption measurement is the *excess adsorption*, also known variously as the *surface excess*, the *Gibbs excess* or the *Gibbsian surface excess*. This quantity is the difference between the actual amount of adsorbate present in the adsorbed layer and that which would be present in the layer if it had the same density as the bulk gas phase, at the particular measurement temperature and pressure. This is illustrated schematically in Figure 6; the region (*a*) in the lower plot is the excess adsorption. An important, and well known, difficulty in the comparison of theoretically calculated or modelled adsorbed quantities and experimental data is the conversion of theoretical gas sorption capacities, expressed as the *total adsorption* (region (*a* + *b*) in Figure 6), to the experimentally measured *excess adsorption*, or vice versa. Although this is perhaps not a direct measurement accuracy problem, the conversion between experimentally determined values and absolute adsorbed quantities lies at the heart of the accurate determination of the hydrogen adsorption capacity of a material and is therefore worth discussing here. So, in this Appendix, we will look at this issue and briefly describe some of the approximations that have been used or proposed in the literature. We will firstly take a look at the definition of hydrogen uptake quantities, and the definitions of the total, or absolute, adsorption and the excess adsorption.

10.2 Definition of Uptake Quantities in a Hydrogen Storage Context

The most frequently quoted quantity, in terms of storage applications, is wt.% (the weight percent capacity). This is the gravimetric storage density of a material. The US Department of Energy (DOE) hydrogen storage target is commonly quoted as a weight percentage, as this is a crucial figure, although the gravimetric storage density is not the only important criterion. The gravimetric target is also the figure for a complete storage device or "system", which is difficult to define. However, we are interested here in the assessment of material properties and so the definition of a storage system, or similar, is beyond the scope of this discussion.

10.2.1 Hydrogen Absorption

Let us start by looking at the case of hydrides, as the storage capacities of these materials are more clearly defined, or are easier to define. The gravimetric capacity of a hydride material is typically calculated from the ratio of the mass of hydrogen stored within the metal or compound to the mass of the host material including the hydrogen [4], so that the capacity in wt.%, $C_{wt.\%}$, is given by,

$$C_{wt.\%} = \left(\frac{\left(H/M \right) M_H}{M_{Host} + \left(H/M \right) M_H} \times 100 \right) \% \qquad \text{(A1)}$$

where H/M = the hydrogen-to-metal or material host atom ratio, M_H = the molar mass of hydrogen, and M_{Host} = the molar mass of the host material or metal. Note that M_{Host} should be calculated for a mole of host atoms, rather than a mole of molecular formula units of the host, by dividing the total molecular weight by the number of atoms in a formula unit, if and where appropriate. The alternative is to use the ratio of hydrogen atoms to formula units for H/M.

10.2.2 Hydrogen Adsorption

The analogous calculation for a hydrogen adsorbent is not possible because of the difficulty in defining the total adsorbed quantity of hydrogen, and therefore the problem of knowing exactly how much hydrogen can be attributed to the adsorbed layer. A typical unit for the excess adsorption in adsorption measurement is the number of moles of adsorbate per unit mass of adsorbent; for example, mol g^{-1}, mmol g^{-1}, or μmol g^{-1} (mol g^{-1} are the units recommended in the IUPAC guidelines [27]). As the molar mass of the adsorbate is known, this can easily be converted into a wt.% uptake but this is not the same as the wt.% uptake definition for hydride materials. The gravimetric uptake can also be seen expressed in terms of the adsorbate mass (mg g^{-1}) and adsorbate volume (cm^3 (STP) g^{-1}), although these units are interchangeable[36]. A calculation equivalent to Eq. (A1) can be made in which the excess adsorption is included in the denominator [220],

$$C_{wt.\%} = \left(\frac{n_a M_H}{n_{Host} M_{Host} + n_a M_H} \times 100 \right) \% \qquad \text{(A2)}$$

where n_a = the excess adsorption in moles and n_{Host} = the number of moles of host material in the sample. However, this still does not account for the total amount of adsorbed hydrogen.

The definition of the volumetric storage density of an adsorbent material is perhaps even more problematic. The volumetric storage density of a hydride is based on the number of hydrogen atoms that can be accommodated in the host structure per unit volume, whether the hydrogen is an interstitial or otherwise forms part of the host structure[37]. Reliably expressing the volumetric storage density of an adsorbent, on the other hand, must take account of the volume occupied by the solid, as well as the pore volume (the volume that would be occupied by hydrogen gas if there were no gas-solid interactions) and the excess adsorption.

If the purpose of the accurate determination of the hydrogen sorption properties of a potential storage material is to determine its usefulness in a real storage situation, then knowledge of both its volumetric and gravimetric storage density is necessary, along with its sorption behaviour at different temperatures and pressures, and so the most important aspect of this area of hydrogen sorption measurement is to use definitions that allow the most effective comparison of different materials and of experimental data. The definition of a volumetric capacity based on the adsorbed surface layer

---

[36] Note that the expression of the gravimetric storage density/capacity in terms of adsorbate volume at STP is not a volumetric uptake, but just an alternative unit for a mole of adsorbate (for example, the volume of 1 mole of an ideal gas at STP = 22.4 l).

[37] The volumetric storage density would not normally include any void volumes in a bed of storage material [4], although in practical engineering terms these will be significant.

volume, or phase density, in this situation may therefore not be particularly useful, as the performance of the material in a real storage situation may be so dependent on other factors, such as the bulk density of the powder bed (taking account of the packing density and packing method, and so on), as to render the volumetric figure effectively meaningless. With these factors in mind, we will now look at some of the definitions of total adsorbed quantities that have appeared in the literature, including those that have been applied to the adsorption of gases other than hydrogen.

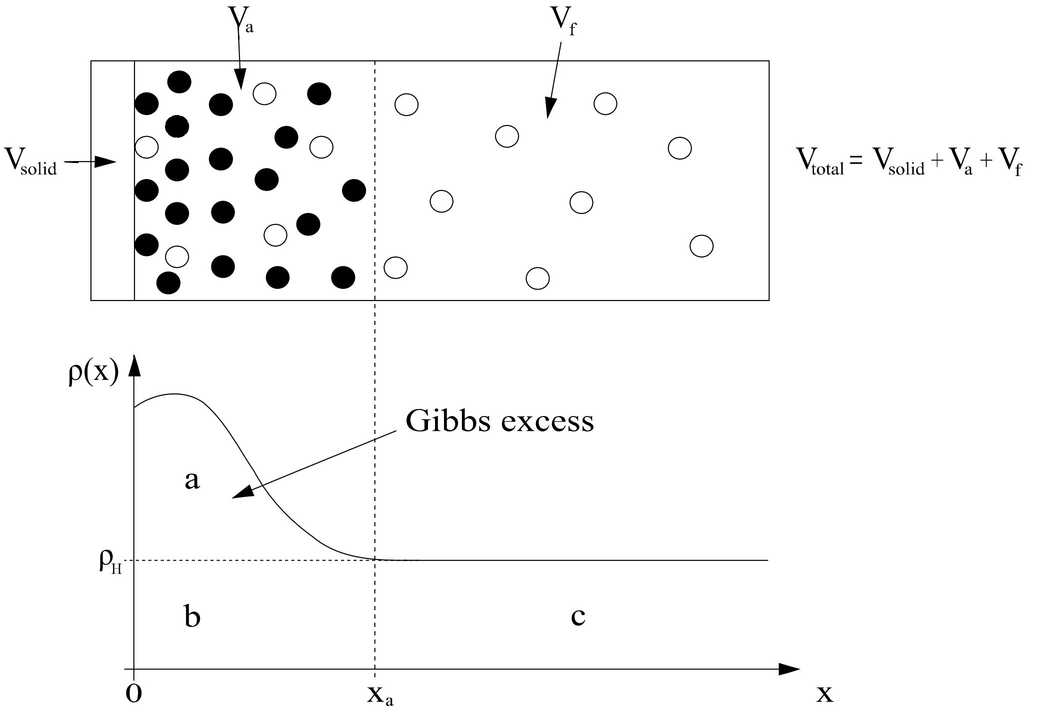


Figure 6. A schematic diagram illustrating the concept of the Gibbs excess and the total adsorbed quantities. The volumes of the solid, V_{solid}, the adsorbed layer, V_a, and the bulk fluid (gas) phase, V_f, are shown. In this diagram, the adsorbed phase volume, V_a, is defined as the volume between the solid surface (at $x = 0$) and the boundary a distance x_a from the surface of the solid. The total fluid (gas) in the system is shown in the lower plot as the region ($a + b + c$), the Gibbs excess is shown as the region (a) and the total adsorbed quantity is shown by the region ($a + b$). In the upper part of this schematic, the white circles indicate molecules that can be attributed to the region ($b + c$) and the black circles indicate molecules that can be attributed to the Gibbs excess (a). As the hydrogen pressure increases, ρ_H will increase and as the pressure decreases, ρ_H will decrease; at very low pressures, the region (b) may become negligible compared to (a), and in this case $m_{tot} \approx m_a$. At higher pressures the region (b) will become of increasing significance to the total adsorption and then $m_{tot} > m_a$; if, at high pressure, the region (a) becomes insignificant compared to region (b), the surface excess will become zero. At higher pressures still, the excess can become negative.

10.3 The Definition and Estimation of the Total Adsorption

The total adsorbed mass, m_{tot}, can be expressed as,

$$m_{tot} = \int_{V(A)} \rho(\mathbf{x})dV \tag{A3}$$

where $\rho(\boldsymbol{x})$ is the gravimetric sorbate density at a point $\boldsymbol{x} = (x_1, x_2, x_3)$ and $V(A)$ is the volume of a set, A, of adsorbate molecules (in our case, all of the hydrogen molecules that are considered to be in the adsorbate phase) [40]. At a sufficient, but unknown, distance from the adsorbent and/or the adsorbent surface, the hydrogen is assumed to approach an equilibrium state of constant bulk density, ρ_H,

$$\rho_H = \lim_{x \to \infty} \rho(\mathbf{x}) \tag{A4}$$

where ρ_H can be described by an accurate equation of state for gaseous hydrogen (see Section 7.12).

The excess adsorbed mass, m_a, can therefore be expressed as,

$$m_a = \int_{V(A)} (\rho(\mathbf{x}) - \rho_H)dV \tag{A5}$$

This is the difference between the total adsorption, m_{tot}, or the total adsorbed mass, and the mass of the hydrogen that would be present in the volume of the adsorbed layer, $V_a = V(A)$, if there were no surface interactions, or no change in the local hydrogen density due to the presence of the surface, and therefore,

$$m_a = m_{tot} - \rho_H V_a \tag{A6}$$

The conversion between m_a and m_{tot} requires knowledge of V_a, the volume of the adsorbed phase, but this is not known as it cannot be measured experimentally. To add further complication in microporous adsorbents, and many real materials, the adsorbate phase is not a simple 2D layer of a known area and thickness, but is a volume that may be fractal in nature, in the same way as the pore network or structure itself. However, m_a can be measured experimentally and it provides a useful quantification of the amount of hydrogen that will be adsorbed by a material. Furthermore, at lower pressures, when the bulk density of the hydrogen, ρ_H, is low, providing there is a significant amount of adsorption, m_a can be considered as being approximately equal to m_{tot}.

However, for storage applications, which necessarily involve higher pressures, the bulk hydrogen density becomes more significant with increasing pressure, and so $m_a \neq m_{tot}$ in this situation[38]. In the description above the total volume of the adsorbent system, V_{total}, is given by,

---

[38] The condition $m_a \approx m_{tot}$ will generally hold if the adsorbate density is much greater than the bulk phase density, which can also be the case at near and subcritical adsorptive temperatures, as the

$$V_{total} = V_{solid} + V_a + V_f \tag{A7}$$

where V_{solid} = the solid adsorbent volume, V_a = the adsorbed phase volume, and V_f = the bulk fluid (gas) phase volume.

We can now define the following reference quantity,

$$m_{ref} = \rho_H (V_{total} - V_{solid}) \tag{A8}$$

This is the mass of gas phase hydrogen that would occupy the dead volume of the adsorption system at a density of ρ_H, in the absence of adsorption, and this can be defined through the use of a reference gas.

The excess adsorption can then be obtained from,

$$m_a = m_{system} - m_{ref} \tag{A9}$$

where m_{system} is the total mass of hydrogen present in the adsorption system. In this expression we do not distinguish between hydrogen that is in the non-adsorbed gas phase (the *adsorptive*) and the hydrogen that is in the adsorbate phase (the *adsorbate*, or the adsorbate layer).

If we consider volumetric measurement, (V_{total} - V_{solid}) in Eq. (A8) is the dead space volume. Therefore, using the direct route for dead space determination, we can measure this experimentally with helium; or, using the indirect route, we can measure V_{total} experimentally, and calculate V_{solid} using the mass of the sample and an independent sample density determination measurement. m_{system} is known from the number of moles of hydrogen introduced into the system and, therefore, m_a is the experimentally measurable quantity. It is here that errors associated with the assumption of helium being non-interacting are introduced.

To calculate the total or absolute adsorption, we would then need to apply Eq. (A6),

$$m_{tot} = m_a + \rho_H V_a \tag{A10}$$

using an assumed value for V_a or, as we will see below, ($\rho_H V_a$).

One simple approach is to assume that,

$$V_a = V_{pore} \tag{A11}$$

where V_{pore} is the estimated, theoretical, or independently measured pore volume. This assumes that the thickness of the adsorbed layer does not change with increasing pressure and adsorption, and it also relies on the accurate determination of the pore volume of the material, which is somewhat problematic. The validity of this

---

adsorbate will probably form a liquid, but this is not likely to be the case with hydrogen adsorption measurement.

assumption depends on the nature of the material: the pore structures of crystalline adsorbents, such as MOFs and zeolites, are more clearly defined, and are therefore perhaps less susceptible to error than the pore structure of amorphous, or non-crystalline, adsorbents such as activated carbon and microporous polymers.

This assumption, termed the *pore volume approximation* by Murata et al [46], was used by Zhou et al [66] in their recent work on the uptake of hydrogen and methane by MOF materials, using the volumetric technique, and by Furukawa et al [99] in their recent volumetric and gravimetric comparative MOF study.

Murata et al [46], in a paper in which they propose their own determination method for absolute, or total, adsorption, reviewed the previous approaches that have been taken towards this problem. In addition to the *pore volume approximation*, they describe the *van der Waals constant approximation*, the *liquid density approximation*, the *critical density approximation* and the *effective thickness approximation*. The model they introduce is termed the *Adsorbed Volume Mapping method*. They also classify the effective thickness and total pore volume approximations as *constant volume methods*, and the van der Waals constant, liquid density and critical density approximations as *constant density methods*.

10.3.1 Constant Volume Methods

The total pore volume approximation is defined by Eq. (A11). The other constant volume method, the effective thickness approximation, uses,

$$V_a = 2\sigma S \tag{A12}$$

where σ = the molecular diameter of the adsorbate and S = the specific surface area of the adsorbent.

In both cases, ρ_H, the bulk gas phase density of hydrogen is used in Eq. (A10) and so the difference between the total adsorption and the surface excess follows the bulk gas phase hydrogen density, which is multiplied by a constant volume term.

One consideration in the assessment of the validity of the assumption, in both of these cases, is the importance of both the surface area and the pore volume in the uptake of hydrogen by an adsorbent. In recent modelling work using GCMC simulations of the total adsorbed quantity of hydrogen by a series of ten MOF structures at 77K, Frost et al [221] show strong evidence for the existence of three adsorption regimes in these materials. At low pressures the uptake correlates with the heat of adsorption, at intermediate pressures it correlates with surface area and at higher pressures it correlates with the free volume (the available pore volume). In this work, low pressure is of the order of 0.01 MPa (0.1 bar), intermediate pressure is of the order of 3 MPa (30 bar) and high pressure is around 12 MPa (120 bar). This would suggest that, in the case of MOFs, an assumption of an adsorbate layer of constant thickness, calculated using the specific surface area of the material, and remaining the same over the entire pressure range is not particularly sound, and that the pore volume approximation is more appropriate in this case, particularly considering that the difference between m_a and m_{tot} becomes increasingly significant at the higher pressures at which the pore volume of the material appears to dominate the total adsorption.

10.3.2 Constant Density Methods

In the other group of approximations, a constant value for the mean adsorbate phase density $\langle \rho_a \rangle$, at a particular temperature, is used. A value for V_a is not used in these expressions although it can be calculated from,

$$V_a = \frac{m_{tot}}{\langle \rho_a \rangle} \tag{A13}$$

The approximations then differ in the expressions used for $\langle \rho_a \rangle$. The critical density approximation uses,

$$\langle \rho_a \rangle = \rho_c \tag{A14}$$

where ρ_c = the critical density of the adsorbate.

The liquid density approximation either uses,

$$\langle \rho_a \rangle = \rho_{liq} \tag{A15}$$

where ρ_{liq} = the liquid density of the adsorbate.

Or,

$$\langle \rho_a \rangle = \frac{\rho_{liq}^{b}}{(\exp[\alpha(T - T_b)])} \tag{A16}$$

where ρ_{liq}^{b} = the liquid density at boiling temperature T_b, and α = a thermal expansion coefficient of superheated liquid.

The van der Waals constant approximation uses,

$$\langle \rho_a \rangle = \frac{M}{b} = \frac{MRT_c}{8P_c} \tag{A17}$$

where b = the van der Waals constant, M = the molar mass, R = the gas constant, T_c = the critical temperature and P_c = the critical pressure.

In these constant density approximations ρ_H is expressed in terms of the fugacity, f,

$$\rho_H = \frac{Mf}{RT} \tag{A18}$$

Using Eq. (A13), the total or absolute adsorption, as a function of fugacity, is then given by,

$$m_{tot}(f) = m_a(f) + \left(\frac{Mf}{RT}\right)\left(\frac{m_{tot}}{\langle \rho_a \rangle}\right) \tag{A19}$$

And therefore,

$$m_{tot} = \frac{m_a(f)}{\left(1 - \frac{Mf}{RT\langle \rho_a \rangle}\right)} \tag{A20}$$

Various methods that can be used for the estimation of total adsorbed quantity, including those described above, were also reviewed by Agarwal and Schwarz [73] in their high pressure gravimetric study of the sub- and supercritical adsorption of methane, ethane, ethylene, propane, carbon dioxide and nitrogen on activated carbon, although their categorization is different to the one described above. In their work, they determine characteristic adsorption curves for the adsorbates using a pseudo vapour pressure above the critical temperature. For a given temperature, T, this pseudo vapour pressure, P_s, can be determined either by extrapolating the Antoine equation,

$$\ln(P_s) = B - \frac{C}{(D+T)} \tag{A21}$$

where B, C and D are empirical coefficients, or by using an expression introduced by Dubinin [222],

$$P_s = \left(\frac{T}{T_c}\right)^2 P_c \tag{A22}$$

They conclude that for the determination of the characteristic curve the choice of pseudo vapour pressure extrapolation method had a more significant effect on the results than the choice of adsorbed phase volume. Of the three temperature-dependent expressions for the adsorbed phase volume that were tested it was not possible to draw a definite conclusion as to the more favourable option.

It is worth noting here that, apart from some notable exceptions [64,66,88,93], the measurement of the temperature dependence of hydrogen adsorption by porous materials is not particularly common. Hydrogen adsorption isotherms are more often determined at a fixed temperature of 77 K, using a dewar of liquid nitrogen, although the temperature dependence of adsorption is of prime importance to the application of adsorbent materials as storage media. This area, including the determination of the absolute adsorbed quantity as a function of temperature and pressure, therefore appears to have significant further research potential.

11 APPENDIX B: PROPOSED MEASUREMENT CHECKLISTS

11.1 Introduction

This Appendix includes proposed checklists for the gas phase measurement of hydrogen adsorption and absorption by materials using the volumetric (manometric or Sieverts) and gravimetric methods. Although considerations relating to the material type are of crucial importance, the following sets of proposed guidelines, which are based on the discussion in Section 7 of this report, are an attempt to provide a summary of the sources of error in each category of measurement. All of these points are open to discussion and this Appendix does not constitute a formal set of guidelines.

11.2 Hydrogen Adsorption

11.2.1 Volumetric

The following summary of the experimental considerations and error sources in the measurement of supercritical hydrogen adsorption by microporous adsorbents using volumetric, or manometric, apparatus applies to measurements made in the temperature range from low temperatures, in the region of 77 K, up to ambient. An upper pressure range is not stated; however, particular attention must be paid to the validity of the equation of state for hydrogen throughout the pressure range of interest at the measurement temperature. It is worth stating that for solid state storage applications the pressures of interest are not particularly high and are ultimately limited by the level at which solid state storage loses its advantage over high pressure hydrogen storage, in terms of safety, and the necessary construction of high strength, lightweight storage vessels. This is of the order of 10 MPa (hundreds of bars).

Error Source / Experimental Consideration	Guidelines
(i) Calibration	Volume, temperature sensor and pressure measuring device calibration are essential. The sample cell dead space volume must be determined to sufficient accuracy.
(ii) Temperature Monitoring and Control	The temperature of the calibrated dosing volumes (the gas delivery system) should be thermostatted and/or room temperature fluctuations monitored carefully. Sample environment (for example, a water or refrigerant bath, a cryofurnace, or liquid nitrogen or argon) temperature should be controlled to an acceptable level. Cold or hot spots in the dosing volumes and hot spots in the sample cell should be eliminated. The region of apparatus containing the temperature gradient must be minimized and

	accounted for in the calculation of the adsorbed quantity.
(iii) Sample Temperature Measurement	The temperature sensor can be in direct contact with sample, and should be monitored continually throughout the measurement.
(iv) Thermal Effects from the Sample	Thermal effects from the sample will not be severe but this may depend on bed size. Sample temperature should be monitored through each sorption step to ensure that the temperature has returned to equilibrium.
(v) Approach to Equilibrium	If sorption is a pure physisorption process, it will be relatively rapid (within minutes) but pressure relaxation should be monitored at each step. Longer timescale changes could be indicative of a problem such as leakage or gas contamination (for example, the chemisorption of impurities or the adsorption of impurities of larger molecular size or lower diffusivity).
(vi) Sample Size Choice	Should be large enough to allow accurate mass determination in an external balance, for example > 50 mg, but should ideally be matched to the system volume and the pressure measurement accuracy. The sample size should not be large enough to cause temperature inhomogeneity problems. The measurement of different sample sizes should not result in different wt.% uptakes; if this is the case it could indicate problems with the sample size choice and/or the sensitivity of the system. It is the degassed sample mass (see point (ix)) that should be used for the calculation of measured uptake.
(vii) Gas Purity	Ideally ≥ 99.9999 %. Filtration (for example, a zeolite for moisture and activated carbon for hydrocarbons/other environmental contaminants, or a liquid nitrogen trap) should be included if gas delivery lines are present. The filter system should be regenerated regularly. An oil-free pumping station is essential to eliminate additional contamination.
(viii) System Volume to Sample Size Ratio	For a given sample size, the system volume must be small enough for the pressure measuring device to detect the required or expected drop in pressure at a given adsorption or desorption step, but not so small that the pressure drop required for a given sample size is too large, as this may lead to larger compressibility errors. Note that it is the system volume (the combined dosing and sample cell volume) that is important, not just the dosing volume.
(ix) Sample Degassing	Should be performed under high vacuum conditions, for example < 10 mPa (10^{-4} mbar) at, or above, the sample. Depending on apparatus geometry, this is likely to require < 100 μPa (10^{-6} mbar) at the vacuum

	pump inlet. The degassing temperature must be high enough to remove any environmental, or other, adsorbates from the sample surface and pore network, without causing significant physical or chemical changes to the sample. Mass loss during sample degassing should be accounted for in the calculation of the measured uptake.
(x) Sample Pretreatment and History	Must be recorded as it can have significant effects on the measured uptake. Full sample details should be included to enable the comparison of data, including sample synthesis details, and sufficient microstructural characterisation of the starting material or compound. The activation procedure, including the degassing pressure (vacuum level), temperature and time, should also be recorded. If two measurements on a sample are to be compared, the degassing/activation procedures used must be comparable.
(xi) Pressure Measurement	The uncertainty in the pressure measurement should be substantially lower than the difference in pressures before and after a typical adsorption or desorption step.
(xii) The Compressibility of Hydrogen	Should be represented accurately, using for example the 32-term modified Benedict-Webb-Rubin (BWR) equation (see the NIST Standard Reference Database 23) or the Soave-Redlich-Kwong (SRK) EOS.
(xiii) Thermal Transpiration Effects	If accurate measurements are to be measured at low pressures (for example < 100 Pa, depending on apparatus dimensions) corrections should be applied to pressure data using an accepted expression (for example, Takaishi and Sensui [208]).
(xiv) Accumulative Errors	Accumulative errors are a likely error source. Their presence can be tested by measuring isotherms with different step sizes, or comparing single step measurements with complete isotherms.
(xv) Leakage	Thorough leak testing should be carried out with helium and/or hydrogen [218] up to the maximum measurement pressure.

11.2.2 Gravimetric

The following summary of the experimental considerations and error sources in the measurement of supercritical hydrogen adsorption by microporous adsorbents using gravimetric apparatus applies to measurements made in the temperature range from low temperatures, in the region of 77 K, up to ambient. An upper pressure range is not stated; however, in gravimetric measurement, particular attention must be paid to the application of buoyancy effect corrections as these increase significantly with increasing pressure (or hydrogen density). The sample density value used in the buoyancy effect corrections must be chosen with care. Attention should also be paid to the validity of the equation of state for hydrogen used throughout the pressure range of interest at the measurement temperature.

Error Source / Experimental Consideration	Guidelines
(i) Calibration	Microbalance, temperature sensor and pressure measuring device calibration are essential.
(ii) Temperature Monitoring and Control	The temperature of the microbalance cabinet or enclosure should be well thermostatted. Sample environment (for example, a water or refrigerant bath, cryofurnace, or liquid nitrogen or argon) temperature should be controlled to an acceptable level.
(iii) Sample Temperature Measurement	The temperature sensor will be in the vicinity of the sample, and should be monitored continually. The temperature measured near to the sample will be affected by the hydrogen pressure in the chamber. Hydrogen has a relatively high thermal conductivity, which may increase the effects. Complementary measurements (for example, thermomagnetometry) can be used to check the correspondence of the sample and measurement temperatures.
(iv) Thermal Effects from the Sample	Thermal effects from the sample are unlikely to be severe. Sample temperature should be observed through each sorption step to ensure that the temperature has returned to equilibrium. Heat may be dissipated more slowly in a relatively large microbalance chamber, compared to a volumetric instrument sample cell.
(v) Approach to Equilibrium	If sorption is a pure physisorption process, the sorption will be relatively rapid (within minutes) but the mass change should be monitored at each step. Longer timescale changes could be indicative of a problem such as gas contamination (for example, the chemisorption of impurities or the adsorption of impurities of larger molecular size or lower diffusivity).
(iv) Sample Size Choice	This will be determined primarily by the balance capacity and sensitivity. Accurate degassed sample mass determination is possible for very small masses but the sample size should not be reduced too far (for example < 50 mg, for a balance of < 1 μg resolution) due to the low molecular mass of hydrogen, although this depends to a certain extent on the expected hydrogen uptake.
(v) Gas Purity	Ideally ≥ 99.9999 %. Filtration (for example, a zeolite for moisture and activated carbon for hydrocarbons/other environmental contaminants, or a liquid nitrogen trap) should be included if gas

	delivery lines are present. The filter system should be regenerated regularly. An oil-free pumping station is essential to eliminate additional contamination.
(vi) Sample Degassing	Should be performed under high vacuum conditions, for example < 10 mPa (10^{-4} mbar) at, or above, the sample. Depending on apparatus geometry, this is likely to require < 100 µPa (10^{-6} mbar) at the vacuum pump inlet. The degassing temperature must be high enough to remove any environmental, or other, adsorbates from the sample surface and pore network, without causing significant physical or chemical changes to the sample. Mass loss should be monitored during degassing to determine when degassing has been completed to a sufficient degree.
(vii) Sample Pretreatment and History	Must be recorded as it can have significant effects on the measured uptake. Full sample details should be included to enable the comparison of data, including sample synthesis details, and sufficient microstructural characterisation of the starting material or compound. The activation procedure, including the degassing pressure (vacuum level), temperature and time, should also be recorded. If two measurements on a sample are to be compared, the degassing/activation procedures used must be comparable.
(viii) Pressure Measurement	The pressure measurement is not as crucial to the measurement of the adsorbed quantity as it is in volumetric measurement, but must still be measured to sufficient accuracy.
(ix) The Compressibility of Hydrogen	Should be represented accurately, using for example the 32-term modified Benedict-Webb-Rubin (BWR) equation (see the NIST Standard Reference Database 23) or the Soave-Redlich-Kwong (SRK) EOS.
(x) Thermal Transpiration Effects	If accurate measurements are to be measured at low pressures (for example, < 100 Pa, depending on apparatus dimensions) corrections should be applied to pressure data using an accepted expression (for example, Takaishi and Sensui [208]). Thermomolecular flow disturbances of the balance should also be monitored and/or determined.
(xi) Buoyancy Effect Corrections	Buoyancy effect corrections must be applied to the measured data to take account of the displacement of the hydrogen by the sample, the sample holder and the balance hangdown, and any other components attached to the balance. The density of hydrogen at the measurement temperature and pressure must be represented accurately (see point (ix)).
(xii) Leakage	Thorough leak testing should be carried out with helium and/or hydrogen [218] up to the maximum measurement pressure.

11.3 Hydrogen Absorption

11.3.1 Volumetric

The following summary of the experimental considerations and error sources in the measurement of hydrogen absorption by hydrogen-absorbing materials using volumetric, or manometric, apparatus (the Sieverts Method) applies to measurements made in the temperature range from ambient to high temperatures in the region of 673 K. An upper pressure range is not stated; however, particular attention must be paid to the validity of the equation of state for hydrogen throughout the pressure range of interest at the measurement temperature.

Error Source / Experimental Consideration	Guidelines
(i) Calibration	Volume, temperature sensor and pressure measuring device calibration are essential. The sample cell dead space volume must be determined to sufficient accuracy.
(ii) Temperature Monitoring and Control	The temperature of the calibrated dosing volumes (the gas delivery system) should be thermostatted and/or room temperature fluctuations monitored carefully. Sample environment (for example, a water bath or furnace) temperature should be controlled to an acceptable level. Cold or hot spots in the dosing volumes and cold spots in the sample cell should be eliminated. The region of apparatus containing the temperature gradient must be minimized and accounted for in the calculation of the absorbed quantity.
(iii) Sample Temperature Measurement	The temperature sensor can be in direct contact with sample, and should be monitored continually throughout the measurement.
(iv) Thermal Effects from the Sample	Thermal effects from the sample may be severe, depending partially on bed size. The sample temperature should therefore be monitored carefully through each sorption step to ensure that it has returned to equilibrium, once a sufficient amount of hydrogen has been absorbed or desorbed by the sample.
(v) Approach to Equilibrium	The pressure relaxation should be monitored at each absorption or desorption step to ensure that the sample has reached equilibrium, or at least an acceptable level of equilibrium. The temperature should also be monitored (see point (iv)).
(vi) Sample Size Choice	Should be large enough to allow accurate mass determination, for example > 50 mg, but should ideally be matched to the size of the system volume and the pressure measurement accuracy. The sample size must not be too large as to allow significant

	thermal inhomogeneity (therefore bed sizes greater than a few grams should be avoided). The measurement of different sample sizes should not result in different wt.% uptakes; if this is the case it could indicate problems with the sample size choice and/or the sensitivity of the system.
(vii) Gas Purity	A minimum of 99.999 %, although the criterion may be higher (for example > 99.9995 %) for more sensitive materials. Filtration should be considered, in the case of more sensitive samples, particularly if gas delivery lines are present. If present, the filter system should be regenerated regularly. An oil-free pumping station is essential to eliminate additional contamination.
(viii) System Volume to Sample Size Ratio	For a given sample size, the system volume must be small enough for the pressure measuring device to detect the required or expected drop in pressure at a given absorption or desorption step, but not so small that the pressure drop required for a given sample size is too large, as this may lead to larger compressibility errors. Note that it is the system volume (the combined dosing and sample cell volume) that is important, not just the dosing volume.
(ix) Sample Degassing	Should be performed under vacuum conditions sufficient to remove environmental adsorbates that may inhibit the initial activation process.
(x) Sample Pretreatment and History	Must be recorded as it can have significant effects on the measured uptake. Full sample details should be included to enable the comparison of data, including sample synthesis details, and sufficient microstructural characterisation of the starting material or compound. The activation procedure should be described (for example, degassing procedure, hydrogen pressures and temperatures, number of cycles, or the mechanical activation procedure, and so forth). If two measurements on the same material are to be compared, the degassing/activation procedures used must be comparable.
(xi) Pressure Measurement	The uncertainty in the pressure measurement should be substantially lower than the difference in pressures before and after an absorption or desorption step.
(xii) The Compressibility of Hydrogen	Should be represented accurately, using for example the 32-term modified Benedict-Webb-Rubin (BWR) equation (see the NIST Standard Reference Database 23) or the Hemmes et al EOS [204].
(xiii) Thermal Transpiration Effects	If accurate measurements are to be performed at low pressures (for example < 100 Pa, depending on apparatus dimensions) corrections should be applied to pressure data using an accepted expression (for

	example, Takaishi and Sensui [208], or Wallbank and McQuillan [206]).
(xiv) Accumulative Errors	Accumulative errors are a likely error source. Their presence can be tested by measuring isotherms with different step sizes, or comparing single step measurements with complete isotherms. However, material-related effects should also be taken into consideration.
(xv) Leakage	Thorough leak testing should be carried out with helium and/or hydrogen [218] up to the maximum measurement pressure.

11.3.2 Gravimetric

The following summary of the experimental considerations and error sources in the measurement of hydrogen absorption by hydrogen-absorbing materials using gravimetric apparatus applies to measurements made in the temperature range from ambient to high temperatures in the region of 673 K. An upper pressure range is not stated; however, in gravimetric measurement, particular attention must be paid to the application of buoyancy effect corrections as these increase significantly with increasing pressure (or hydrogen density). The sample density value used in the buoyancy effect corrections must be chosen with care. Attention should also be paid to the validity of the equation of state for hydrogen used throughout the pressure range of interest at the measurement temperature.

Error Source / Experimental Consideration	Guidelines
(i) Calibration	Microbalance, temperature sensor and pressure measuring device calibration are essential.
(ii) Temperature Monitoring and Control	The temperature of the microbalance cabinet or enclosure should be well thermostatted. Sample environment (for example, a water bath or furnace) temperature should be controlled to an acceptable level.
(iii) Sample Temperature Measurement	The temperature sensor will be in the vicinity of the sample, and should be monitored continually. The temperature measured near to the sample will be affected by the hydrogen pressure in the chamber. Hydrogen has a relatively high thermal conductivity, which may increase the effects. Complementary measurements (for example, thermomagnetometry) can be used to check the correspondence of the sample and measurement temperatures.
(iv) Thermal Effects from the Sample	Thermal effects from the sample may be severe. The sample temperature should therefore be monitored through each sorption step to ensure that it has returned to equilibrium, once a sufficient amount of hydrogen has been absorbed or desorbed by the sample.

(v) Approach to Equilibrium	The mass change should be monitored carefully at each absorption step to ensure that the sample has reached equilibrium, or at least an acceptable level of equilibrium. The temperature should also be monitored (see point (iv)).
(vi) Sample Size Choice	This will be determined primarily by the balance capacity and sensitivity. Accurate sample mass determination is possible for very small masses but the sample size should not be reduced too far (for example < 50 mg, for a balance of < 1 μg resolution) due to the low mass of hydrogen, although this depends to a certain extent on the expected hydrogen uptake.
(vii) Gas Purity	A minimum of 99.999 %, although the criterion may be higher (for example > 99.9995 %) for more sensitive materials. Filtration should be considered, in the case of more sensitive samples, particularly if gas delivery lines are present. If present, the filter system should be regenerated regularly. An oil-free pumping station is essential to eliminate additional contamination.
(viii) Sample Degassing	Should be performed under vacuum conditions sufficient to remove environmental adsorbates that may inhibit the initial activation process.
(ix) Sample Pretreatment and History	Must be recorded as it can have significant effects on the measured uptake. Full sample details should be included to enable the comparison of data, including sample synthesis details, and sufficient microstructural characterisation of the starting material or compound. The activation procedure should be described (for example, degassing procedure, hydrogen pressures and temperatures, number of cycles, or the mechanical activation procedure, and so forth). If two measurements on the same material are to be compared, the degassing/activation procedures used must be comparable.
(x) Pressure Measurement	The pressure measurement is not as crucial to the measurement of the absorbed quantity as it is in volumetric measurement, but must still be measured to sufficient accuracy.
(xi) The Compressibility of Hydrogen	Should be represented accurately, using for example the 32-term modified Benedict-Webb-Rubin (BWR) equation (see the NIST Standard Reference Database 23) or the Hemmes et al EOS [204].
(xii) Thermal Transpiration Effects	If accurate measurements are to be measured at low pressures (for example < 100 Pa, depending on apparatus dimensions) corrections should be applied to pressure data using an accepted expression (for example, Takaishi and Sensui [208], or Wallbank and

	McQuillan [206]). Thermomolecular flow disturbances of the balance should also be monitored and/or determined.
(xiii) Buoyancy Effect Corrections	Buoyancy effect corrections must be applied to the measured data to take account of the displacement of the hydrogen by the sample, the sample holder and the balance hangdown, and any other components attached to the balance. The density of hydrogen at the measurement temperature and pressure must be represented accurately (see point (xi)).
(xiv) Leakage	Thorough leak testing should be carried out with helium and/or hydrogen [218] up to the maximum measurement pressure.

12 REFERENCES

[1] Tzimas E., Filiou C., Peteves S. D., Veyret J. –B., *Hydrogen storage: state-of-the-art and future perspective* 2003: EUR 20995 EN, European Commission, The Netherlands, ISBN 92-894-6950-1 (2003)

[2] Broom D. P., "The accuracy of hydrogen sorption measurements on potential storage materials" *International Journal of Hydrogen Energy* 32 (2007) 4871-4888

[3] Eberle U., Arnold G., von Helmholt R., "Hydrogen storage in metal-hydrogen systems and their derivatives" *Journal of Power Sources* 154 (2006) 456-460

[4] Sandrock G., "A panoramic overview of hydrogen storage alloys from a gas reaction point of view" *Journal of Alloys and Compounds* 293-295 (1999) 877-888

[5] Schlapbach L., Züttel A., "Hydrogen-storage materials for mobile applications" *Nature* 414 (2001) 353-358

[6] Grochala W., Edwards P. P., "Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen" *Chemical Reviews* 104(3) (2004) 1283-1315

[7] Schüth F., Bogdanović B., Felderhoff M., "Light metal hydrides and complex hydrides for hydrogen storage" *Chemical Communications* 20 (2004) 2249-2258

[8] Sakintuna B., Lamari-Darkrim F., Hirscher M., "Metal hydride materials for solid hydrogen storage: A review" *International Journal of Hydrogen Energy* 32 (2007) 1121-1140

[9] Orimo S., Nakamori Y., Eliseo J. R., Züttel A., Jensen C. M., "Complex hydrides for hydrogen storage" *Chemical Reviews* 107(10) (2007) 4111-4132

[10] Langmi H. W., McGrady G. S., "Non-hydride systems of the main group elements as hydrogen storage materials" *Coordination Chemistry Reviews* 251(7-8) (2007) 925-935

[11] Thomas K. M., "Hydrogen adsorption and storage on porous materials" *Catalysis Today* 120(3-4) (2007) 389-398

[12] Hodoshima S., Arai H., Saito Y., "Liquid-film-type catalytic decalin dehydrogeno-aromatization for long-term storage and long-distance transportation of hydrogen" *International Journal of Hydrogen Energy* 28 (2003) 197-204

[13] Schlapbach L., "Surface properties and activation" In: Schlapbach L. (editor) *Topics in applied physics Vol. 67: Hydrogen in intermetallic compounds II* Springer-Verlag, Berlin (1992) p. 15-95

[14] Fukai Y., *The metal-hydrogen system: basic bulk properties* (2nd Edition) Springer-Verlag, Berlin (2005)

[15] Alefeld G., Völkl J., (editors) *Topics in applied physics Vol. 28: Hydrogen in metals I. Basic properties* Springer-Verlag, Berlin (1978)

[16] Alefeld G., Völkl J., (editors) *Topics in applied physics Vol. 29: Hydrogen in metals II. Application-oriented properties* Springer-Verlag, Berlin (1978)

[17] Schlapbach L., (editor) *Topics in applied physics Vol. 63: Hydrogen in intermetallic compounds I. Electronic, thermodynamic and crystallographic properties, preparation* Springer-Verlag, Berlin (1988)

[18] Schlapbach L., (editor) *Topics in applied physics Vol. 67: Hydrogen in intermetallic compounds II. Surface and dynamic properties, applications* Springer-Verlag, Berlin (1992)

[19] Wipf H., (editor) *Topics in applied physics Vol. 73: Hydrogen in metals III. Properties and applications* Springer-Verlag, Berlin (1997)

[20] Sandrock G., Bowman Jr R. C., "Gas-based hydride applications: recent progress and future needs" *Journal of Alloys and Compounds* 356-357 (2003) 794-799

[21] Reilly J. J., Adzic G. D., Johnson J. R., Vogt T., Mukerjee S., McBreen J., "The correlation between composition and electrochemical properties of metal hydride electrodes" *Journal of Alloys and Compounds* 293-295 (1999) 569-582

[22] Cuevas F., Joubert J. M., Latroche M., Percheron-Guégan A., "Intermetallic compounds as negative electrodes of Ni/MH batteries" *Applied Physics A* 72 (2001) 225-238

[23] Joubert J. M., Latroche M., Percheron-Guégan A., "Metallic Hydrides II: Materials for Electrochemical Storage" *MRS Bulletin* 27(9) (2002) 694-698

[24] Keller J. U., Robens E., "A note on sorption measuring instruments" *Journal of Thermal Analysis and Calorimetry* 71 (2003) 37-45

[25] British Standards Institution, *Determination of the specific surface area of powders - Part 4: Recommendations for methods of determination of metal surface area using gas adsorption techniques* BS 4359-4 (1996)

[26] Rouquérol F., Rouquérol J., Sing K., *Adsorption by powders and porous solids: principles, methodology and applications* Academic Press, London (1999)

[27] Sing K. S. W., Everett D. H., Haul R. A. W., Moscou L., Pierotti R. A., Rouquérol J., Siemieniewska T., "Reporting physisorption data for gas/solid systems - with special reference to the determination of surface area and porosity" *Pure and Applied Chemistry* 57(4) (1985) 603-619

[28] Aranovich G., Donohue M., "Analysis of adsorption isotherms: Lattice theory predictions, classification of isotherms for gas-solid equilibria, and similarities in gas and liquid adsorption behaviour" *Journal of Colloid and Interface Science* 200 (1998) 273-290

[29] Bogdanov A. A., "On the limiting physical adsorption of hydrogen in carbon materials" *Technical Physics* 50(9) (2005) 139-142

[30] Zhou L., "Progress in fundamental research into supercritical adsorption and its impact on clean energy technology" *Adsorption Science and Technology* 23(7) (2005) 509-518

[31] Wilson T., Tyburski A., DePies M. R., Vilches O. E., Becquet D., Bienfait M., "Adsorption of H_2 and D_2 on carbon nanotube bundles" *Journal of Low Temperature Physics* 126(1-2) (2002) 403-408

[32] Diehl L. M. A., Chaves F. A. B., Lerner E., "Multilayer adsorption isotherms of para-hydrogen on graphite" *Journal of Low Temperature Physics* 92(3-4) (1993) 173-180

[33] Mistura G., Lee H. C., Chan M. H. W., "Hydrogen adsorption on alkali metal surfaces: wetting, prewetting and triple-point wetting" *Journal of Low Temperature Physics* 96(5-6) (1994) 221-244

[34] Yildirim T., Hartman M. R., "Direct observation of hydrogen adsorption sites and nanocage formation in metal-organic frameworks" *Physical Review Letters* 95 (2005) 215504

[35] Cole M. W., Hernández E. S., "Unified theory of adsorption, pore-filling and wetting" *Physical Review B* 75 (2007) 205421

[36] Malbrunot P., Vidal D., Vermesse J., Chahine R., Bose T. K., "Adsorption measurements of argon, neon, krypton, nitrogen, and methane on activated carbon up to 650MPa" *Langmuir* 8 (1992) 577-580

[37] Ustinov E. A., Do D. D., Herbst A., Staudt R., Harting P., "Modeling of gas adsorption equilibrium over a wide range of pressure: A thermodynamic approach based on equation of state" *Journal of Colloid and Interface Science* 250 (2002) 49-62

[38] Myers A. L., "Thermodynamics of adsorption in porous materials" *AIChE Journal* 48(1) (2002) 145-160

[39] Lozano-Castelló D., Cazorla-Amorós D., Linares-Solano A., "Usefulness of CO_2 adsorption at 273K for the characterization of porous carbons" *Carbon* 42 (2004) 1233-1242

[40] Keller J. U., Staudt R., *Gas adsorption equilibria: experimental methods and adsorptive isotherms* Springer, New York (2005)

[41] Keller J. U., Robens E., du Fresne von Hohenesche C., "Thermogravimetric and Sorption Measurement Techniques/Instruments" *Studies in Surface Science and Catalysis* 144 (2002) 387-394

[42] Luo S., Clewley J. D., Flanagan T. B., Bowman Jr R. C., Wade L. A., "Further studies of the isotherms of $LaNi_{5-x}Sn_x$-H for x = 0-0.5" *Journal of Alloys and Compounds* 267 (1998) 171-181

[43] Huhn P. -A., Dornheim M., Klassen T., Bormann R., "Thermal stability of nanocrystalline magnesium for hydrogen storage" *Journal of Alloys and Compounds* 404-406 (2005) 499-502

[44] Japanese Industrial Standards Committee, *Glossary of terms used in hydrogen absorbing alloys* JIS H 7003 (1989)

[45] Bojon J. P., Hilleret N., Weiss K., "Origin of possible contamination introduced by a turbomolecular pumping system" *Vacuum* 53 (1999) 247-251

[46] Murata K., El-Merraoui M., Kaneko K., "A new determination method of absolute adsorption isotherm of supercritical gases under high pressure with a special relevance to density-functional theory study" *Journal of Chemical Physics* 114(9) (2001) 4196-4205

[47] Neimark A. V., Ravikovitch P. I., "Calibration of pore volume in adsorption experiments and theoretical models" *Langmuir* 13 (1997) 5148-5160

[48] Malbrunot P., Vidal D., Vermesse J., Chahine R., Bose T. K., "Adsorbent helium density measurement and its effect on adsorption isotherms at high pressure" *Langmuir* 13 (1997) 539-544

[49] Sircar S., "Measurement of Gibbsian Surface Excess" *AIChE Journal* 47(5) (2001) 1170-1176

[50] Gérard N., Belkbir L., Joly E., "High-accuracy volumetric device for hydrogen sorption kinetic studies" *Journal of Physics E: Scientific Instruments* 12 (1979) 476-477

[51] Percheron-Guégan A., Lartigue C., Achard J. C., "Correlations between the structural properties, the stability and the hydrogen content of substituted $LaNi_5$ compounds" *Journal of the Less-Common Metals* 109 (1985) 287-309

[52] Checchetto R., Trettel G., Miotello A., "Sievert-type apparatus for the study of hydrogen storage in solids" *Measurement Science and Technology* 15 (2004) 127-130

[53] Blach T. P., Gray E. Mac A., "Sieverts apparatus and methodology for accurate determination of hydrogen uptake by light-atom hosts" *Journal of Alloys and Compounds* 446-447 (2007) 692-697

[54] Reilly J. J., Wiswall R. H., "The reaction of hydrogen with alloys of magnesium and copper" *Inorganic Chemistry* 6(12) (1967) 2220-2223

[55] Reilly J. J., Wiswall R. H., "The reaction of hydrogen with alloys of magnesium and nickel and the formation of Mg_2NiH_4" *Inorganic Chemistry* 7(11) (1968) 2254-2256

[56] Reilly J. J., Wiswall R. H., "The higher hydrides of vanadium and niobium" *Inorganic Chemistry* 9(7) (1970) 1678-1682

[57] Blackledge J. P., "Chemistry of metal hydrides as related to their applications in nuclear technology" In: Mueller W. M., Blackledge J. P., Libowitz G. G., (editors) *Metal hydrides* Academic Press, London (1968) p. 119-164

[58] Bowman Jr R. C., Luo C. H., Ahn C. C., Witham C. K., Fultz B., "The effect of tin on the degradation of $LaNi_{5-y}Sn_y$ metal hydrides during thermal cycling" *Journal of Alloys and Compounds* 217 (1995) 185-192

[59] Borghard W. S., Sheppard E. W., Schoennagel H. J., "An automated, high precision unit for low-pressure physisorption" *Review of Scientific Instruments* 62(11) (1991) 2801-2809

[60] Maglara E., Pullen A., Sullivan D., Conner W. C., "Characterisation of microporous solids by adsorption: measurement of high-resolution adsorption isotherms" *Langmuir* 10 (1994) 4167-4173

[61] Kiyoyabashi T., Takeshita H. T., Tanaka H., Takeichi N., Züttel A., Schlapbach L., Kuriyama N., "Hydrogen adsorption in carbonaceous materials – How to determine the storage capacity accurately" *Journal of Alloys and Compounds* 330-332 (2002) 666-669

[62] Poirier E., Chahine R., Tessier A., Bose T. K., "Gravimetric and volumetric approaches adapted for hydrogen sorption measurements with *in-situ* conditioning on small sorbent samples" *Review of Scientific Instruments* 76 (2005) 055101

[63] Panella B., Hirscher M., "Hydrogen physisorption in metal-organic porous crystals" *Advanced Materials* 17(5) (2005) 538-541

[64] Panella B., Hirscher M., Pütter H., Müller U., "Hydrogen adsorption in metal-organic frameworks: Cu-MOFs and Zn-MOFs compared" *Advanced Functional Materials* 16 (2006) 520-524

[65] Dailly A., Vajo J. J., Ahn C. C., "Saturation of hydrogen sorption in Zn benzenedicarboxylate and Zn naphthalenedicarboxylate" *Journal of Physical Chemistry B* 110(3) (2006) 1099-1101

[66] Zhou W., Wu H., Hartman M. R., Yildirim T., "Hydrogen and methane adsorption in metal-organic frameworks: A high-pressure volumetric study" *Journal of Physical Chemistry C* 111(44) (2007) 16131-16137

[67] Panella B., Kossykh L., Dettlaff-Weglikowska U., Hirscher M., Zerbi G., Roth S., "Volumetric measurement of hydrogen storage in HCL-treated polyaniline and polypyrrole" *Synthetic Metals* 151 (2005) 208-210

[68] Vajo J. J., Mertens F., Ahn C. C., Bowman Jr R. C., Fultz B., "Altering hydrogen storage properties by hydride destabilization through alloy formation: LiH and MgH_2 destabilized with Si" *Journal of Physical Chemistry B* 108(37) (2004) 13977-13983

[69] Sandrock G., Gross K., Thomas G., Jensen C., Meeker D., Takara S., "Engineering considerations in the use of catalyzed sodium alanates for hydrogen storage" *Journal of Alloys and Compounds* 330-332 (2002) 696-701

[70] Gross K. J., Thomas G. J., Jensen C. M., "Catalyzed alanates for hydrogen storage" *Journal of Alloys and Compounds* 330-332 (2002) 683-690

[71] Gast Th., Robens E., "Modern Vacuumbalances" *Journal of Thermal Analysis* 47 (1996) 605-617

[72] Robens E., Gast T., Hoinkis E., Müller U., "Surface area, density and porosity measurements using the magnetic suspension balance" *Fresenius Zeitschrift für Analytische Chemie* 333 (1989) 428-432

[73] Agarwal R. K., Schwarz J. A., "Analysis of high pressure adsorption of gases on activated carbon by potential theory" *Carbon* 26(6) (1988) 873-887

[74] Robens E., Gast Th., Straube B., "Applications of buoyancy" *Thermochimica Acta* 152 (1989) 149-156

[75] Robens E., "Physical adsorption studies with the vacuum microbalance" *Journal of Vacuum Science and Technology* 17(1) (1980) 92-97

[76] Stonadge P. R., Benham M. J., Ross D. K., Manwaring C., Harris I. R., "The measurement of concentration dependent diffusion coefficients in the solid-solution alloy Pd-Y" *Zeitschrift für Physikalische Chemie, Bd.* 181 (1993) S125-131

[77] Buckley C. E., Gray E. Mac A., Kisi E. H., "Stability of the hydrogen absorption and desorption plateaux in $LaNi_5$-H. Part 1: Hysteresis dynamics and location of the equilibrium isotherm" *Journal of Alloys and Compounds* 215 (1994) 195-199

[78] Gray E. Mac A., Blach T. P., Buckley C. E., "Stability of the hydrogen absorption and desorption plateaux in $LaNi_5$-H. Part 5: H capacity" *Journal of Alloys and Compounds* 293-295 (1999) 57-61

[79] Rasmussen M. D., Akinc M., "Microcomputer-controlled gravimetric adsorption apparatus" *Review of Scientific Instruments* 11 (1983) 1558-1564

[80] Astill D. M., Hall P. L., McConnell J. D. C., "An automated vacuum microbalance for measurement of adsorption isotherms" *Journal of Physics E: Scientific Instruments* 20 (1987) 19-21

[81] Thompson K. A., Fuller Jr E. L., "Computer-controlled vacuum microbalance techniques for surface area and porosity measurements" *Langmuir* 3 (1987) 699-703

[82] Akporiaye D., Plassen M., "An up-to-date automated instrument for the characterization of microporous/mesoporous solids" *Review of Scientific Instruments* 68(5) (1997) 2111-2115

[83] Zuech J. L., Hines A. L., Sloan E. D., "Methane adsorption on 5A molecular sieve in the pressure range 4 to 690 kPa" *Industrial and Engineering Chemistry Process Design and Development* 22 (1983) 172-174

[84] De Weireld G., Frère M., Jadot R., "Automated determination of high-temperature and high-pressure gas adsorption isotherms using a magnetic suspension balance" *Measurement Science and Technology* 10 (1999) 117-126

[85] Lutz H. M., Schmitt R., Steffens F., "A high-temperature, high-pressure microbalance for the determination of the hydrogen sorption characteristics of metal hydrides" *Thermochimica Acta* 24 (1978) 369-381

[86] Benham M. J., Ross D. K., "Experimental determination of absorption-desorption isotherms by computer-controlled gravimetric analysis" *Zeitschrift für Physikalische Chemie, NF* 163 (1989) S25-32

[87] Ansón A., Benham M., Jagiello J., Callejas M. A., Benito A. M., Maser W. K., Züttel A., Sudan P., Martínez M. T., "Hydrogen adsorption on a single-walled carbon nanotube material: a comparative study of three different adsorption techniques" *Nanotechnology* 15 (2004) 1503-1508

[88] Zhao X., Xiao B., Fletcher A. J., Thomas K. M., Bradshaw D., Rosseinsky M. J., "Hysteretic adsorption and desorption of hydrogen by nanoporous metal-organic frameworks" *Science* 306 (2004) 1012-1015

[89] Lin X., Jia J., Zhao X., Thomas K. M., Blake A. J., Walker G. S., Champness N. R., Hubberstey P., Schröder M., "High H_2 adsorption by coordination-framework materials" *Angewandte Chemie International Edition* 45 (2006) 7358–7364

[90] Xiao B., Wheatley P. S., Zhao X., Fletcher A. J., Fox S., Rossi A. G., Megson I. L., Bordiga S., Regli L., Thomas K. M., Morris R. E., "High-capacity hydrogen and nitric oxide adsorption and storage in a metal-organic framework" *Journal of the American Chemical Society* 129 (2007) 1203-1209

[91] Langmi H. W., Walton A., Al-Mamouri M. M., Johnson S. R., Book D., Speight J. D., Edwards P. P., Gameson I., Anderson P. A., Harris I. R., "Hydrogen adsorption in zeolites A, X, Y and RHO" *Journal of Alloys and Compounds* 356-357 (2003) 710-715

[92] Langmi H. W., Book D., Walton A., Johnson S. R., Al-Mamouri M. M., Speight J. D., Edwards P. P., Harris I. R., Anderson P. A., "Hydrogen storage in ion-exchanged zeolites" *Journal of Alloys and Compounds* 404-406 (2005) 637-642

[93] Zhao X. B., Xiao B., Fletcher A. J., Thomas K. M., "Hydrogen adsorption on functionalized nanoporous activated carbons" *Journal of Physical Chemistry B* 109 (2005) 8880-8888

[94] McKeown N. B., Gahnem B., Msayib K. J., Budd P. M., Tattershall C. E., Mahmood K., Tan S., Book D., Langmi H. W., Walton A., "Towards polymer-based hydrogen storage materials: engineering ultramicroporous cavities within polymers of intrinsic microporosity" *Angewandte Chemie International Edition* 45 (2006) 1804-1807

[95] Lee J. -Y., Wood C. D., Bradshaw D., Rosseinsky M. J., Cooper A. I., "Hydrogen adsorption in microporous hypercrosslinked polymers" *Chemical Communications* 25 (2006) 2670-2672

[96] Wood C. D., Tan B., Trewin A., Niu H., Bradshaw D., Rosseinsky M. J., Khimyak Y. Z., Campbell N. L., Kirk R., Stöckel E., Cooper A. I., "Hydrogen storage in microporous hypercrosslinked organic polymer networks" *Chemistry of Materials* 19 (2007) 2034-2048

[97] Ghanem B. S., Msayib K. J., McKeown N. B., Harris K. D. M., Pan Z., Budd P. M., Butler A., Selbie J., Book D., Walton A., "A triptycene-based polymer of intrinsic microporosity that displays enhanced surface area and hydrogen adsorption" *Chemical Communications* 1 (2007) 67-69

[98] Budd P. M., Butler A., Selbie J., Mahmood K., McKeown N. B., Ghanem B., Msayib K., Book D., Walton A., "The potential of organic polymer-based hydrogen storage materials" *Physical Chemistry Chemical Physics* 9(15) (2007) 1802-1808

[99] Furukawa H., Miller M. A., Yaghi O. M., "Independent verification of the saturation hydrogen uptake in MOF-177 and establishment of a benchmark for hydrogen adsorption in metal-organic frameworks" *Journal of Materials Chemistry* 17 (2007) 3197-3204

[100] Bhattacharya M., Devi W. G., Mazumdar P. S., "Determination of kinetic parameters from temperature programmed desorption curves" *Applied Surface Science* 218 (2003) 1-6

[101] Bhatia S., Beltramini I., Do D. D., "Temperature-programmed analysis and its applications in catalytic systems" *Catalysis Today* 7 (1990) 309-438

[102] Ma M. C., Brown T. C., Haynes B. S., "Evaluation of thermal desorption spectra for heterogeneous surfaces: application to carbon surface oxides" *Surface Science* 297 (1993) 312-326

[103] Kowalczyk P., Kaneko K., Terzyk A. P., Tanaka H., Kanoh H., Gauden P. A., "New approach to determination of surface heterogeneity of adsorbents and catalysts from the temperature programmed desorption (TPD) technique: One step beyond the condensation approximation (CA) method" *Journal of Colloid and Interface Science* 291 (2005) 334-344

[104] Kanervo J. M., Keskitalo T. J., Slioor R. I., Krause A. O. I., "Temperature-programmed desorption as a tool to extract quantitative kinetic or energetic information for porous catalysts" *Journal of Catalysis* 238 (2006) 382-393

[105] Ulbricht H., Zacharia R., Cindir N., Hertel T., "Thermal desorption of gases and solvents from graphite and carbon nanotube surfaces" *Carbon* 44 (2006) 2931-2942

[106] Brown M. E., *Introduction to thermal analysis: techniques and applications* (2nd edition) Kluwer Academic Publishers, Dordrecht (2001)

[107] Materazzi S., "Mass spectrometry coupled to thermogravimetry (TG-MS) for evolved gas characterisation: a review" *Applied Spectroscopy Reviews* 33(3) (1998) 219-236

[108] Stern A., Kreitzman S. R., Resnik A., Shaltiel D., Zevin V., "Thermal desorption spectra of hydrogen from the bulk ZrV_2H_x" *Solid State Communications* 40 (1981) 837-841

[109] Castro F. J., Meyer G., "A novel thermal desorption spectroscopy apparatus" *Review of Scientific Instruments* 71(5) (2000) 2131-2133

[110] von Zeppelin F., Haluška M., Hirscher M., "Thermal desorption spectroscopy as a quantitative tool to determine the hydrogen content in solids" *Thermochimica Acta* 404 (2003) 251-258

[111] Turnbull A., Hutchings R. B., Ferriss D. H., "Modelling of thermal desorption of hydrogen from metals" *Materials Science and Engineering A* 238 (1997) 317-328

[112] Yamaguchi T., Nagumo M., "Simulation of hydrogen thermal desorption under reversible trapping by lattice defects" *ISIJ International* 43(4) (2003) 514-519

[113] Tal-Gutelmacher E., Eliezer D., Abramov E., "Thermal desorption spectroscopy (TDS) - Application in quantitative study of hydrogen evolution and trapping in crystalline and non-crystalline materials" *Materials Science and Engineering A* 445-446 (2007) 625-631

[114] Hatton P. J., Southward B. W. L., "Optimisation of the connection between TA-MS systems together with improved data interpretation for TA-MS applications" *Journal of Thermal Analysis and Calorimetry* 72 (2003) 83-92

[115] Panella B., Hirscher M., Ludescher B., "Low-temperature thermal-desorption mass spectroscopy applied to investigate the hydrogen adsorption on porous materials" *Microporous and Mesoporous Materials* 103(1-3) (2007) 230-234

[116] Castro F. J., Sanchez A. D., Meyer G., "Bulk effects in thermal desorption spectroscopy" *Journal of Chemical Physics* 109(16) (1998) 6940-6946

[117] Castro F. J., Meyer G., "Thermal desorption spectroscopy (TDS) method for hydrogen desorption characterization (I): theoretical aspects" *Journal of Alloys and Compounds* 330-332 (2002) 59-63

[118] Gabis I., Evard E., Voyt A., Chernov I., Zaika Yu., "Kinetics of decomposition of erbium hydride" *Journal of Alloys and Compounds* 356-357 (2003) 353-357

[119] Stern A., Resnik A., Shaltiel D., "Thermal desorption spectra of hydrogen in HfV_2H_x and ZrV_2H_x" *Journal of the Less-Common Metals* 88 (1982) 431-440

[120] Mendelsohn M. H., Gruen D. M., "Temperature-programmed desorption (TPD) studies of $ZrV_{1.6}Fe_{0.4}H_y$ and $ZrV_{1.2}Cr_{0.8}H_y$" *Materials Research Bulletin* 16 (1981) 1027-1034

[121] Stern A., Resnik A., Shaltiel D., "Thermal desorption spectra of the PdH_x system in a powder form" *Journal of Physics F: Metal Physics* 14 (1984) 1625-1639

[122] Resnik A., Stioui M., Grayevsky A., Shaltiel D., "Thermal desorption spectra of hydrogen from $LaNi_5$" *Journal of the Less-Common Metals* 131 (1987) 117-124

[123] Hall P. J., Berlouis L. E. A., Mackinnon A. J., Wilson J., Browning D., Dodd S., Morris S., Jones P., Calo J. M., "Analysis of FeTi hydride alloys by thermal analysis, small angle neutron scattering and positron annihilation" *Journal of Alloys and Compounds* 253-254 (1997) 195-200

[124] Fernández J. F., Cuevas F., Sánchez C., "Simultaneous differential scanning calorimetry and thermal desorption spectroscopy measurements for the study of the decomposition of metal hydrides" *Journal of Alloys and Compounds* 298 (2000) 244-253

[125] Maciejewski M., Baiker A., "Quantitative calibration of mass spectrometric signals measured in coupled TA-MS system" *Thermochimica Acta* 295 (1997) 95-105

[126] Kaiserberger E., Post E., "Practical aspects for the coupling of gas analytical methods with thermal-analysis instruments" *Thermochimica Acta* 295 (1997) 73-93

[127] Ichikawa T., Hanada N., Isobe S., Leng H. Y., Fujii H., "Hydrogen storage properties in Ti catalysed Li-N-H system" *Journal of Alloys and Compounds* 404-406 (2005) 435-438

[128] Riktor, M. D., Sørby M. H., Chłopek K., Fichtner M., Buchter F., Züttel A., Hauback B. C., "*In situ* synchrotron diffraction studies of phase transitions and thermal decomposition of $Mg(BH_4)_2$ and $Ca(BH_4)_2$" *Journal of Materials Chemistry* 17 (2007) 4939-4942

[129] Dillon A. C., Jones K. M., Bekkedahl T. A., Kiang C. H., Bethune D. S., Heben M. J., "Storage of hydrogen in single-walled carbon nanotubes" *Nature* 386 (1997) 377-379

[130] Züttel A., Orimo S., "Hydrogen in nanostructured, carbon-related, and metallic materials" *MRS Bulletin* 27(9) (2002) 705-711

[131] Hirscher M., Becher M., Haluska M., Quintel A., Skakalova V., Choi Y. -M., Dettlaff-Weglikowska U., Roth S., Stepanek I., Bernier P., Leonhardt A., Fink J., "Hydrogen storage in carbon nanostructures" *Journal of Alloys and Compounds* 330-332 (2002) 654-658

[132] Avraham I., Danon A., Koresh J. E., "Study of carbon molecular sieve fibres by atmospheric TPD-MS of H_2O, CO and CO_2" *Journal of the Chemical Society, Faraday Transactions* 94(13) (1998) 1869-1874

[133] Züttel A., Nützenadel Ch., Sudan P., Mauron Ph., Emmenegger Ch., Rentsch S., Schlapbach L., Weidenkaff A., Kiyobayashi T., "Hydrogen sorption by carbon nanotubes and other carbon nanostructures" *Journal of Alloys and Compounds* 330-332 (2002) 676-682

[134] Cohen R. L., West K. W., Wernick J. H., "Degradation of $LaNi_5$ hydrogen-absorbing material by cycling" *Journal of the Less-Common Metals* 70 (1980) 229-241

[135] Lambert S. W., Chandra D., Cathey W. N., Lynch F. E., Bowman Jr R. C., "Investigation of hydriding properties of $LaNi_{4.8}Sn_{0.2}$, $LaNi_{4.27}Sn_{0.24}$ and $La_{0.9}Gd_{0.1}Ni_5$ after thermal cycling and aging" *Journal of Alloys and Compounds* 187 (1992) 113-135

[136] Beeri O., Cohen D., Gavra Z., Johnson J. R., Mintz M. H., "High-pressure studies of the $TiCr_{1.8}$-H_2 system Statistical thermodynamics above the critical temperature" *Journal of Alloys and Compounds* 267 (1998) 113-120

[137] Schefer R. W., Houf W. G., San Marchi C., Chernicoff W. P., Englom L., "Characterization of leaks from compressed hydrogen dispensing systems and related components" *International Journal of Hydrogen Energy* 31 (2006) 1247-1260

[138] San Marchi C., Somerday B. P., Robinson S. L., "Permeability, solubility and diffusivity of hydrogen isotopes in stainless steels at high gas pressures" *International Journal of Hydrogen Energy* 32 (2007) 100-116

[139] Chambers A., Park C., Baker R. T. K., Rodriguez N. M., "Hydrogen storage in graphite nanofibers" *Journal of Physical Chemistry B* 102(22) (1998) 4253-4256

[140] Becher M., Haluska M., Hirscher M., Quintel A., Skakalova V., Dettlaff-Weglikovska U., Chen X., Hulman M., Choi Y., Roth S., Meregalli V., Parrinello M., Ströbel R., Jörissen L., Kappes M. M., Fink J., Züttel A., Stepanek I., Bernier P., "Hydrogen storage in carbon nanotubes" *Comptes Rendus Physique* 4 (2003) 1055-1062

[141] Lamari Darkrim F., Malbrunot P., Tartaglia G. P., "Review of hydrogen storage by adsorption in carbon nanotubes" *International Journal of Hydrogen Energy* 27 (2002) 193-202

[142] Han J. I., Lee J. Y., "The effect of CO impurity on the hydrogenation properties of $LaNi_5$, $LaNi_{4.7}Al_{0.3}$ and $MmNi_{4.5}Al_{0.5}$ during hydriding-dehydriding cycling" *Journal of the Less-Common Metals* 152 (1989) 319-327

[143] *International vocabulary of basic and general terms in metrology* ISBN 92-67-01075-1 (1993)

[144] Currie L. A., Svehla G., "Nomenclature for the presentation of results of chemical analysis (IUPAC Recommendations 1994)" *Pure and Applied Chemistry* 66(3) (1994) 595-608

[145] Cox M. G., Harris P. M., "Measurement uncertainty and traceability" *Measurement Science and Technology* 17 (2006) 533-540

[146] ASTM International, *Standard practice for conducting an interlaboratory study to determine the precision of a test method* E 691-99 (1999)

[147] Graham T., "On the absorption and dialytic separation of gases by colloid septa" *Philosophical Transactions of the Royal Society of London* 156 (1866) 399-439

[148] Manchester F. D., San-Martin A., Pitre J. M., "The H-Pd (Hydrogen-Palladium) System" *Journal of Phase Equilibria* 15(1) (1994) 62-83

[149] Mütschele T., Kirchheim R., "Segregation and diffusion of hydrogen in grain boundaries of palladium" *Scripta Metallurgica* 21 (1987) 135-140

[150] Mütschele T., Kirchheim R., "Hydrogen as a probe for the average thickness of a grain boundary" *Scripta Metallurgica* 21 (1987) 1101-1104

[151] Thomas G. J., Siegel R. W., Eastman J. A., "Grain boundaries in nanophase palladium: high resolution electron microscopy and image simulation" *Scripta Metallurgica et Materialia* 24 (1990) 201-206

[152] Kuji T., Matsumura Y., Uchida H., Aizawa T., "Hydrogen absorption of nanocrystalline palladium" *Journal of Alloys and Compounds* 330-332 (2002) 718-722

[153] Huot J., Liang G., Schulz R., "Mechanically alloyed metal hydride systems" *Applied Physics A* 72 (2001) 187-195

[154] Westlake D. G., "Hydrides of intermetallic compounds: a review of stabilities, stoichiometries and preferred hydrogen sites" *Journal of the Less-Common Metals* 91 (1983) 1-20

[155] Suleiman M., Jisrawi N. M., Dankert O., Reetz M. T., Bähtz C., Kirchheim R., Pundt A., "Phase transition and lattice expansion during hydrogen loading of nanometer sized palladium clusters" *Journal of Alloys and Compounds* 356-357 (2003) 644-648

[156] Snyder R. L., Fiala J., Bunge H. J., (editors) *Defect and microstructure analysis by diffraction* Oxford University Press, Oxford (1999)

[157] Rowsell J. L. C., Eckert J., Yaghi O. M., "Characterization of H_2 binding sites in prototypical metal-organic frameworks by inelastic neutron scattering" *Journal of the American Chemical Society* 127 (2005) 14904-14910

[158] Neumann D. A., "Neutron scattering and hydrogenous materials" *Materials Today* 9(1-2) (2006) 34-41

[159] Rowsell J. L. C., Yaghi O. M., "Metal-organic frameworks: a new class of porous materials" *Microporous and Mesoporous Materials* 73 (2004) 3-14

[160] Rowsell J. L. C., Yaghi O. M., "Strategies for hydrogen storage in metal-organic frameworks" *Angewandte Chemie International Edition* 44 (2005) 4670-4679

[161] Sing K. S. W., "Adsorption methods for the characterization of porous materials" *Advances in Colloid and Interface Science* 76-77 (1998) 3-11

[162] Aranovich G. L., Donohue M. D., "Adsorption isotherms for microporous adsorbents" *Carbon* 33(10) (1995) 1369-1375

[163] Japanese Industrial Standards Committee, *Method of determining the PCT relations of hydrogen-absorbing alloys* JIS H 7201 (1991)

[164] Japanese Industrial Standards Committee, *Method for determining the hydriding rate of hydrogen-absorbing alloys* JIS H 7202 (1993)

[165] Japanese Industrial Standards Committee, *Method for assessing the characteristics of cyclic hydrogen absorption/desorption of hydrogen absorbing alloys* JIS H 7203 (1995)

[166] Japanese Industrial Standards Committee, *Method for measuring the heat of hydriding reaction of hydrogen absorbing alloys* JIS H 7204 (1995)

[167] British Standards Institution, *Determination of the specific surface area of powders - Part 1: BET method of gas adsorption for solids (including porous materials)* BS 4359-1:1996 (ISO 9277:1995) (1996)

[168] Belmabkhout Y., Frère M., De Weireld G., "High-pressure adsorption measurements. A comparative study of the volumetric and gravimetric methods" *Measurement Science and Technology* 15 (2004) 848-858

[169] Wang X. –L., Suda S., "Consistent determination of the intrinsic kinetic properties between hydrogen and hydriding alloys" *Journal of Alloys and Compounds* 231(1-2) (1995) 660-665

[170] Gray E. Mac A., Buckley C. E., Kisi E. H., "Stability of the hydrogen absorption and desorption plateaux in $LaNi_5$-H. Part 2: Effects of absorbing and desorbing large aliquots of hydrogen" *Journal of Alloys and Compounds* 215(1-2) (1994) 201-211

[171] Kisi E. H., Gray E. Mac A., "Stability of the hydrogen absorption and desorption plateaux in $LaNi_5$-H. Part 3: experimental observations of compositional inhomogeneities due to temperature gradients" *Journal of Alloys and Compounds* 217 (1995) 112-117

[172] Buckley C. E., Gray E. Mac A., Kisi E. H., "Stability of the hydrogen absorption and desorption plateaux in $LaNi_5$-H. Part 4: thermal history effects" *Journal of Alloys and Compounds* 231 (1995) 460-466

[173] Zhang C., Lu X., Gu A., "How to accurately determine the uptake of hydrogen in carbonaceous materials" *International Journal of Hydrogen Energy* 29 (2004) 1271-1276

[174] Zhou L., Zhou Y., "Determination of compressibility factor and fugacity coefficient of hydrogen in studies of adsorptive storage" *International Journal of Hydrogen Energy* 26 (2001) 597-601

[175] Tibbetts G. G., Meisner G. P., Olk C. H., "Hydrogen storage capacity of carbon nanotubes, filaments, and vapour-grown fibers" *Carbon* 39 (2001) 2291-2301

[176] Hirscher M., Becher M., Haluska M., von Zeppelin F., Chen X., Dettlaff-Weglikowska U., Roth S., "Are carbon nanostructures an efficient hydrogen storage medium?" *Journal of Alloys and Compounds* 356-357 (2003) 433-437

[177] Blackman J. M., Patrick J. W., Snape C. E., "An accurate volumetric differential pressure method for the determination of hydrogen storage capacity at high pressures in carbon materials" *Carbon* 44 (2006) 918-927

[178] Lee Y. -W., Clemens B. M., Gross K. J., "Novel Sieverts' type volumetric measurements of hydrogen storage properties for very small sample quantities" *Journal of Alloys and Compounds* 452(2) (2008) 410-413

[179] Bruno T. J., Svoronos P. D. N., *CRC handbook of basic tables for chemical analysis*, CRC Press, Florida (1989)

[180] Bloch J., Mintz M. H., "Kinetics and mechanisms of metal hydrides formation - a review" *Journal of Alloys and Compounds* 253-254 (1997) 529-541

[181] Goodell P. D., Rudman P. S., "Hydriding and dehydriding rates of the $LaNi_5$-H system" *Journal of the Less-Common Metals* 89 (1983) 117-125

[182] Wang X. -L., Suda S., "Reaction kinetics of metal hydrides under quasi-isothermal conditions" *Journal of the Less-Common Metals* 172-174 (1991) 969-982

[183] Reid C. R., Thomas K. M., "Adsorption kinetics and size exclusion properties of probe molecules for the selective porosity in a carbon molecular sieve used for air separation" *Journal of Physical Chemistry B* 105 (2001) 10619-10629

[184] Flanagan T. B., Oates W. A., "Some thermodynamic aspects of metal hydrogen systems" *Journal of Alloys and Compounds* 404-406 (2005) 16-23

[185] Walton K. S., Snurr R. Q., "Applicability of the BET method for determining surface areas of microporous metal-organic frameworks" *Journal of the American Chemical Society* 129 (2007) 8552-8556

[186] Düren T., Millange F., Férey G., Walton K. S., Snurr R. Q., "Calculating geometric surface areas as a characterization tool for metal-organic frameworks" *Journal of Physical Chemistry C* 111(42) (2007) 15350-15356

[187] Goodell P. D., "Cycling hydriding response of $LaNi_5$ in hydrogen containing oxygen as a minor impurity" *Journal of the Less-Common Metals* 89 (1983) 45-54

[188] Block F. R., Bahs J. -J., "Investigation of selective absorption of hydrogen by $LaNi_5$ and FeTi" *Journal of the Less-Common Metals* 89 (1983) 77-84

[189] Ono S., Ishido Y., Akiba E., Jindo K., Sawada Y., Kitagawa I., Kakutani T., "The effect of CO_2, CH_4, H_2O and N_2 on Mg-Ni alloys as hydrogen transporting media" *International Journal of Hydrogen Energy* 11(6) (1986) 381-387

[190] Sridhar Kumar M. P., Viswanathan B., Swamy C. S., Srinivasan V., "Interaction of carbon monoxide with the hydrogen storage alloy, $CaNi_5$; kinetic and surface studies" *Reactivity of Solids* 7 (1989) 157-166

[191] Amankwah K. A. G., Schwarz J. A., "Assessment of the effect of impurity gases on the storage capacity of hydrogen on activated carbon using the concept of effective adsorbed phase molar volume" *International Journal of Hydrogen Energy* 16(5) (1991) 339-344

[192] Pedersen A. S., Larsen B., "The storage of industrially pure hydrogen in magnesium" *International Journal of Hydrogen Energy* 18(4) (1993) 297-300

[193] Bouaricha S., Huot J., Guay D., Schulz R., "Reactivity during cycling of nanocrystalline Mg-based hydrogen storage compounds" *International Journal of Hydrogen Energy* 27 (2002) 909-913

[194] Goodell P. D., "Stability of rechargeable hydriding alloys during extended cycling" *Journal of the Less-Common Metals* 99 (1984) 1-14

[195] Dabrowski A., Robens E., Klobes P., Meyer K., Podkościelny P., "Standardization of methods for characterizing the surface geometry of solids" *Particle and Particle Systems Characterisation* 20 (2003) 311-322

[196] Reid C. R., Thomas K. M., "Adsorption of gases on a carbon molecular sieve used for air separation: linear adsorptives as probes for kinetic selectivity" *Langmuir* 15 (1999) 3206-3218

[197] Redhead P. A., "Recommended practices for measuring and reporting outgassing data" *Journal of Vacuum Science and Technology A* 20(5) (2002) 1667-1675

[198] Lafferty J. M., (editor) *Foundations of Vacuum Science and Technology* John Wiley & Sons, New York (1998)

[199] Robens E., Krebs K. -F., Meyer K., Unger K. K., Dabrowski A., "Progress in the standardization of particle and surface characterisation" *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 208 (2002) 253-257

[200] *Guide to the measurement of pressure and vacuum* National Physical Laboratory, UK ISBN 0 904457 29 X (1998)

[201] Lemmon E. W., Huber M. L., Friend D. G., Paulina C., *Standardized equation for hydrogen gas densities for fuel consumption applications* National Institute of Standards and Technology Report 2006-01-0434. 2006

[202] Lemmon E. W., Huber M. L., McLinden M. O., NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 8.0. National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg (2007)

[203] McLennan K. G., Gray E. Mac A., "An equation of state for deuterium gas to 1000 bar" *Measurement Science and Technology* 15 (2004) 211-215

[204] Hemmes H., Driessen A., Griessen R., "Thermodynamic properties of hydrogen at pressures up to 1 Mbar and temperatures between 100 and 1000K" *Journal of Physics C: Solid State Physics* 19 (1986) 3571-3585

[205] Tkacz M., Litwiniuk A., "Useful equations of state of hydrogen and deuterium" *Journal of Alloys Compounds* 330-332 (2002) 89-92

[206] Wallbank A. D., McQuillan A. D., "Thermal transpiration correction of hydrogen equilibrium pressure measurements in metal/hydrogen solution" *Journal of the Chemical Society, Faraday Transactions 1* 71 (1975) 685-689

[207] Liang S. C., "On the calculation of thermal transpiration" *Journal of Physical Chemistry* 57 (1953) 910

[208] Takaishi T., Sensui Y., "Thermal transpiration effect of hydrogen, rare gases and methane" *Transactions of the Faraday Society* 59 (1963) 2503-2514

[209] Miiller A. P., "Measurement performance of high-accuracy low-pressure transducers" *Metrologia* 36 (1999) 617-621

[210] De Angeli M., Ghezzi F., "Solution for pressure measurement problems in finding PCT equilibrium characteristics of hydrogen getters" *Vacuum* 53 (1999) 257-262

[211] York D. C., Chambers A., Chew A. D., Troup A. P., "Measurement of thermal transpiration across an array of parallel capillaries using a differential capacitance manometer" *Vacuum* 55 (1999) 133-139

[212] York D. C., Chambers A., Chew A. D., "Thermal transpiration of helium and nitrogen in 50-μm bore silica capillaries" *Vacuum* 59 (2000) 910-918

[213] Poulis J. A., Thomas J. M., "Disturbances arising from thermal transpiration in microbalance experiments" *Journal of Scientific Instruments* 40 (1963) 95-100

[214] Poulis J. A., Pelupessy B., Massen C. H., Thomas J. M., "Longitudinal Knudsen forces" *Journal of Scientific Instruments* 41 (1964) 295-301

[215] Poulis J. A., Massen C. H., Thomas J. M., "Longitudinal Knudsen forces II" *Journal of Scientific Instruments* 43 (1966) 234-237

[216] Behrndt K. H., Massen C. H., Poulis J. A., Steensland T., "Longitudinal thermomolecular flow at intermediate pressures - a comparison" In: Behrndt K. H., (editor) *Vacuum Microbalance Techniques, Vol. 5* Plenum Press, New York (1966) p. 33-47

[217] Bley W. G., "Leak detection and leak detectors" In: Lafferty J. M., (editor) *Foundations of Vacuum Science and Technology* John Wiley & Sons, New York (1998) p. 481-506

[218] British Standards Institution *Non-destructive testing - Leak testing - Criteria for method and technique selection* BS EN 1779:1999 (1999)

[219] Lee I. D., Smith O. I., Karagozian A. R., "Hydrogen and helium leak rates from micromachined orifices" *AIAA Journal* 41(3) (2003) 457-464

[220] Garberoglio G., Skoulidas A. I., Johnson J. K., "Adsorption of gases in metal organic materials: comparison of simulations and experiments" *Journal of Physical Chemistry B* 109 (2005) 13094-13103

[221] Frost H., Düren T., Snurr R. Q., "Effects of surface area, free volume, and heat of adsorption on hydrogen uptake in metal-organic frameworks" *Journal of Physical Chemistry B* 110 (2006) 9565-9570

[222] Dubinin M. M., In: Cadenhead D., A., et al, (editors) *Progress in Surface and Membrane Science, Vol. 9, Ch. 1* Academic Press, New York (1975)

European Commission

EUR 23242 EN – Joint Research Centre – Institute for Energy
Title: Hydrogen Sorption Measurements on Potential Storage Materials: Experimental Methods and Measurement Accuracy
Author: D. P. Broom
Luxembourg: Office for Official Publications of the European Communities
2008 – 81 pp. – 21 x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-08345-7
DOI: 10.2790/86100

Abstract

The hydrogen storage problem is one of the major issues that needs to be resolved if hydrogen is to become a viable energy carrier in the future. An earlier EUR report examined the problem, including its possible solution through the use of a solid state storage material. This option is one of the most attractive for a number of reasons, although no material currently satisfies the practical requirements, in terms of storage capacity, operating temperature and pressure ranges, impurity resistance, long term cycling stability and cost. The search for a material that fulfils the criteria for a practical store is therefore generating a great deal of scientific research interest, and an increasing number of publications on this topic are appearing in the scientific literature.

A crucial part of the search for new storage materials is the accurate determination of the hydrogen sorption or storage characteristics of new or modified materials. This is an issue that has come to prominence in recent years due to the controversy over the potential storage capacity of carbon nanostructures, such as nanotubes and nanofibres, during which widely varying claims of potential storage capacity and hydrogen uptake behaviour were made. A significant contribution to this controversy was made by inaccuracy in the measurement of the potential gas phase hydrogen storage capacities of these nanostructured carbon materials.

This report focuses on the gas phase, as opposed to electrochemical, characterisation of the equilibrium hydrogen sorption properties of potential storage materials, and covers the common techniques that can be used to determine the hydrogen uptake behaviour of potential hydrogen storage media. The latter part of the report concentrates on the accuracy of these measurement techniques and discusses the possible sources of error in these methods with reference to previous work that has appeared in the scientific press, as well as existing measurement standards and guidelines. In addition, checklists of the issues that affect the accuracy of hydrogen sorption measurement, in the case of absorbers and adsorbents, based on the discussion presented here, are tentatively proposed. The Appendix also includes a discussion of the conversion of the experimentally-determined hydrogen adsorption parameter, the excess adsorption, to a total, or absolute, adsorbed quantity. The part of this report that addresses measurement accuracy is based on a review article published recently in the International Journal of Hydrogen Energy.

JRC
EUROPEAN COMMISSION

LD- NA- 23242 EN- C

Publications Office
Publications.eu.int

ISBN 978-92-79-08345-7
9 789279 083457