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Isosteric enthalpies for hydrogen adsorbed on nanoporous materials at high pressures

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Abstract A sound understanding of any sorption system requires an accurate determination of the enthalpy of adsorption. This is a fundamental thermodynamic quantity that can be determined from experimental sorption data and its correct calculation is extremely important for heat management in adsorptive gas storage applications. It is especially relevant for hydrogen storage, where porous adsorptive storage is regarded as a competing alternative to more mature storage methods such as liquid hydrogen and compressed gas. Among the most common methods to calculate isosteric enthalpies in the literature are the virial equation and the Clausius–Clapeyron equation. Both methods have drawbacks, for example, the arbitrary number of terms in the virial equation and the assumption of ideal gas behaviour in the Clausius–Clapeyron equation. Although some researchers have calculated isosteric enthalpies of adsorption using excess amounts adsorbed, it is arguably more relevant to applications and may also be more thermodynamically consistent to use absolute amounts adsorbed, since the Gibbs excess is a partition, not a thermodynamic phase. In this paper the isosteric enthalpies of adsorption are calculated using the virial, Clausius–Clapeyron and Clapeyron equations from hydrogen sorption data for two materials—activated carbon AX-21 and metal-organic framework MIL-101. It is shown for these two example materials that the Clausius–Clapeyron equation can only be used at low coverage, since hydrogen's behaviour deviates from ideal at high pressures. The use of the virial equation for isosteric enthalpies is shown to require care, since it is highly dependent on selecting an appropriate number of parameters. A systematic study on the use of different parameters for the virial was performed and it was shown that, for the AX-21 case, the Clausius–Clapeyron seems to give better approximations to the exact isosteric enthalpies calculated using the Clapeyron equation than the virial equation with 10 variable parameters.

Keywords Isosteric enthalpies of adsorption · Hydrogen storage · Thermal management · Storage systems · Porous materials · Physisorption

Abbreviations

bdc	Benzene-1,4-dicarboxylate
BET	Brunauer–Emmett–Teller
DA	Dubinin–Astakhov
DR	Dubinin–Radushkevich
EOS	Equation of state
H–K	Horváth–Kawazoe
IUPAC	International Union of Pure and Applied Chemistry
MOF	Metal-organic framework
MIL	Matérial Institut Lavoisier
TPD	Temperature programmed desorption
RMSR	Root mean squared residual

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List of symbols

a	Adjustable first term parameters for the virial equation
b	Adjustable second term parameters for the virial equation
b_T	Affinity parameter for the Tóth equation
c_T	Heterogeneity parameter for the Tóth equation
$g(n)$	Polynomial function for the isosteres
h	Enthalpy
l	Number of parameters for a in the virial
m	Number of parameters for b in the virial
m_E	Excess mass uptake
m_A	Absolute mass uptake
m_T	Total mass uptake
n	Mass amount adsorbed
n_a	Constant mass amount adsorbed
P	Absolute pressure
Q_{st}	Differential isosteric enthalpy of adsorption
$\overline{Q_{st}}$	Average differential isosteric enthalpy of adsorption
R	Molar gas constant
R^2	Coefficient of determination
s	Entropy
T	Temperature
T_f	Final temperature
T_i	Initial temperature
v	Molar volume
V_A	Volume occupied by the constant density adsorbate
V_P	Total volume in the pore
v_A	Molar volume of the adsorbate
v_B	Molar volume of the bulk adsorptive
wt%	Units for hydrogen uptake as a percentage of sample specific dry mass
Δh	Change in enthalpy
Δs	Change in entropy
θ_A	Fractional filling
ρ_A	Adsorbate mass density
ρ_B	Bulk adsorptive mass density
χ^2_{red}	Reduced Chi squared

1 Introduction

The use of hydrogen as a sustainable, clean, wide-spread energy vector has long been proposed as an alternative to our current energy system, in an attempt to overcome some of the problems caused by the use of fossil fuels. Although the ease in converting energy from fossil fuels and their relative low cost have made them extremely popular and responsible for 85 % of all the primary energy that is produced, there are many associated problems. Their limited availability, their unequal distribution on Earth, and the pollutants they emit when used have long been a cause for worry and they have prompted governments and societies to look for clean, sustainable energy systems, which are likely to be based on renewable sources of energy and using hydrogen as an energy vector (Dorian et al. 2006). However, a number of breakthroughs are still necessary for hydrogen to be used as an energy vector with large-scale utilisation, including issues related to clean production, necessary infrastructure, and efficient and competitive use in fuel cells or heat engines. Of all the necessary breakthroughs, arguably the biggest challenge is the efficient, safe and economic storage of hydrogen for later use (Edwards et al. 2008). This is not only relevant for mobile applications, but also for energy storage purposes in the electric grid (for example storing intermittent renewable electricity), since molecular hydrogen (H_2) occupies large volumes at normal pressures and temperatures due to its exceptionally low density.

There are a number of different storage alternatives being proposed and one of the most interesting prospects for hydrogen storage is adsorbing it on a porous material. Physical adsorption (or physisorption) relies on weak van der Waals forces that enhance the concentration of the gas on the surface of the solid (van den Berg and Arean 2008). Different classes of porous materials have been suggested as hydrogen storage materials, including porous carbons (Yurum et al. 2009), polymers (Dawson et al. 2012) and metal-organic frameworks (MOFs) (Murray et al. 2009).

Significant storage of hydrogen in a porous material only occurs at moderate pressures and cryogenic temperatures (Eberle et al. 2009). A storage system for hydrogen, if based on physisorption, must involve management of ad- and desorption heats, so knowledge of the fundamental thermodynamic variables for the system is essential.

Experimental approaches, including calorimetric methods or temperature programmed desorption (TPD) can provide direct information on the energies of interaction (Matsumoto et al. 2006; Lynch and Flanagan 1974; Leu and Chang 2002; Broom 2011). Calorimetric methods rely on detection of heat released upon the exothermic adsorption event, while TPD detects the desorption of surface-bound species (for example, via changes in pressure or via mass spectrometry) as a function of temperature. Both of these methods have notable drawbacks. They require specialist equipment and were initially applied to studies of chemisorption (e.g., interaction of gaseous hydrogen with metallic catalysts such as Pd black and Al_2O_3-supported Ir (Lynch and Flanagan 1974; Leu and Chang 2002), which generally involve energies of adsorption >30 kJ mol^{-1}. The lower enthalpies associated with pure physisorption (typically ~5–10 kJ mol^{-1} at zero coverage) are difficult to accurately determine, and thus indirect methods of calculating the enthalpies from adsorption isotherms are more commonly used. It has also

been notably difficult to reconcile the enthalpies obtained from calorimetry with isosteric methods, with the different methods yielding different results (Shen et al. 2000).

One indirect method of estimating the enthalpies of adsorption is the isosteric method (Rouquerol et al. 1999). Calculation of the differential isosteric enthalpies of adsorption requires that the isotherms are determined for a number of different temperatures. After this, the isosteres—pressures as a function of temperature for constant amounts adsorbed—are analysed yielding differential isosteric enthalpies. In the literature, this has been done mostly using the Clausius–Clapeyron equation applied to the isosteres (Rouquerol et al. 1999). Another common method for estimating the differential isosteric enthalpies of adsorption involves the use of the virial equation, which fits a polynomial with an adjustable number of parameters to the isotherms and then estimates the isosteric enthalpy of adsorption as a function of coverage (Czepirski and Jagiello 1989). Both methods have their limitations—the virial equation has an arbitrary number of adjustable parameters (which are determined based on the statistical fits to the data) and the Clausius–Clapeyron equation assumes negligible molar volume of the adsorbate and ideal gas adsorptive. These assumptions may not apply at high pressures, especially for supercritical gases, which do not condense and hence do not have a limit for the maximum adsorption pressure. The exact thermodynamic equation for phase changes, the Clapeyron equation, should be used if an accurate calculation of the differential isosteric enthalpy of adsorption is needed (Vuong and Monson 1996; Bimbo et al. 2011). As shown in our previous work, with higher loadings, the enthalpies calculated using the Clapeyron equation deviate from the ones calculated using the Clausius–Clapeyron equation (Bimbo et al. 2011). Also important, the isosteric enthalpies of adsorption are often determined using the excess adsorbed quantity, which due to the difficulty of defining the position of the Gibbs dividing surface, can be considered to be a partition of the adsorbate, rather than a real thermodynamic phase.

To compare the different methods used to calculate adsorption enthalpies, here we use the virial, the Clausius-Clapeyron and the Clapeyron equations to analyse hydrogen excess data. A methodology developed by our research group (Sharpe et al. 2013) and others (Schlichtenmayer and Hirscher 2012), which assumes a constant density of the adsorbate and distinguishes between excess, absolute and total uptake is applied to the data. The calculation of the isosteric enthalpies of adsorption is applied to the absolute uptake of two materials (activated carbon AX-21 and MOF MIL-101, which were tested for high-pressure, cryogenic adsorption of hydrogen), using the virial, the Clausius–Clapeyron and the Clapeyron equation, with the differences in using each method highlighted.

2 Materials and methods

2.1 Materials and characterisation

AX-21 activated carbon was sourced from Anderson Development Company Inc., Michigan USA. It has a Brunauer, Emmett and Teller (BET) 77 K nitrogen specific surface area of 2,448 ± 40 $m^2\ g^{-1}$, a skeletal density of 2.23 g cm^{-3} as measured by helium pycnometry, and a reported micropore volume of 1.03 $cm^3\ g^{-1}$ as determined by the Dubinin–Radushkevich (DR) method (Dubinin et al. 1947; Rouquerol et al. 1999). The reported pore size distribution is relatively narrow, with the majority of the pores around 1.3 nm in diameter (Kluson and Scaife 2001).

MIL-101 is a chromium (III) terephthalate MOF $[Cr_3O(bdc)_3(OH,F)(H_2O)_2]$, (where MIL stands for Matérial Institut Lavoisier, and bdc is benzene-1,4-dicarboxylate) which was first synthesised in the Institut Lavoisier in France (Férey et al. 2005), and was prepared in our laboratories as described in our previous paper (Sharpe et al. 2013). It has a measured BET 77 K nitrogen specific surface area of 2,887 ± 106 $m^2\ g^{-1}$ and a skeletal density of 1.69 g cm^{-3} measured using helium pycnometry. The total pore volume and the micropore volume (diameter below 2 nm) were 1.51 and 0.87 $cm^3\ g^{-1}$, respectively, measured on a full N_2 isotherm at 77 K using the Horváth–Kawazoe (H–K) method (Horvath and Kawazoe 1983). As reported, although there are limitations with this method, especially in the mesopore region (Bae et al. 2009), it is assumed that the H–K is the best method for calculating pore size distributions in MOFs. MIL-101 has a tri-modal pore size distribution consisting of small pores of 0.7 nm, medium pores of 2.9 nm and large pores of 3.4 nm (Streppel and Hirscher 2011).

All BET surface area measurements were obtained using the British Standard Method (British Standards Institution 1996) from low pressure (in the 0.05 to 0.3 P/P_0 range) nitrogen sorption measurements, with a 60 min equilibration time (Hruzewicz-Kolodziejczyk et al. 2012). The skeletal density was measured at room temperature using a helium pycnometer.

2.2 Experimental high pressure hydrogen sorption isotherms

High pressure volumetric gas sorption studies were conducted on a Hiden HTP-1 Sieverts-type volumetric gas sorption analyser (Hiden Isochema, Warrington, UK) up to pressures of 20 MPa. Prior to each measurement, the samples were degassed as described below in order to remove impurities from surfaces and pores. All excess isotherms are reported with the hydrogen uptake on a sample-specific dry mass (wt%), *i.e.,* relative to the degassed sample weight.

Samples of AX-21 (~100 mg) were degassed at 423 K for 12 h prior to measurement of high pressure hydrogen sorption isotherms at 90, 100, 110 and 120 K, up to a maximum pressure of 18 MPa. Samples of MIL-101 (~100 mg) were degassed at 423 K for 4 h prior to measurement of high pressure hydrogen sorption isotherms at 77, 90, 100, 110, 120 and 130 K, up to a maximum pressure of 12 MPa.

The hydrogen excess isotherms for AX-21 and MIL-101 are shown in Figs. 1 and 2, respectively.

2.3 The model to fit to the isotherms

We have previously reported a methodology to analyse supercritical adsorption in a microporous material using the example of hydrogen adsorption on NOTT-101 MOF (Bimbo et al. 2011). This methodology was recently developed to account for a constant density of the adsorbed phase (Sharpe et al. 2013) and distinguishes between total, absolute and excess uptake, in a similar way to the descriptions used by Schlichtenmayer and Hirscher (2012). The total is the total amount of hydrogen within the pore (including the bulk adsorptive), the absolute is the quantity in the adsorbate with constant density within the pore and the excess is the quantity measured in an experiment as the mass or molar enhancement of adsorptive measured in excess of a non-adsorbing probe gas (usually helium). A diagram explaining this is in Fig. 3 showing the density profiles for the three quantities.

The equations that represent the excess, absolute and total adsorption are, respectively:

$$m_E = (\rho_A - \rho_B)\theta_A V_P \quad (1)$$

$$m_A = \rho_A \theta_A V_P \Leftrightarrow m_A = m_E + \rho_B \theta_A V_P \quad (2)$$

$$m_T = \rho_A \theta_A V_P + \rho_B V_P (1 - \theta_A) \Leftrightarrow m_T = m_E + \rho_B V_P \quad (3)$$

For all equations, m_E, m_A and m_T are the excess, absolute and total mass uptake and ρ_A and ρ_B are the adsorbed and bulk mass density of H_2. Rather than a homogeneous density in the pore which increases with increasing pressure, this model assumes that the adsorbate has a constant density and occupies a sample-specific volume V_A. The volume is a fraction of the total sample specific volume V_P, which represents the total volume available in the pore. The ratio of adsorbed volume to total volume varies between 0 and 1 and increases with increasing pressure. It is modelled using the fractional filling θ_A, which, for supercritical adsorption in a microporous material, is assumed to follow a International Union of Pure and Applied Chemistry (IUPAC) type I equation (Sing et al. 1985). There are a number of IUPAC

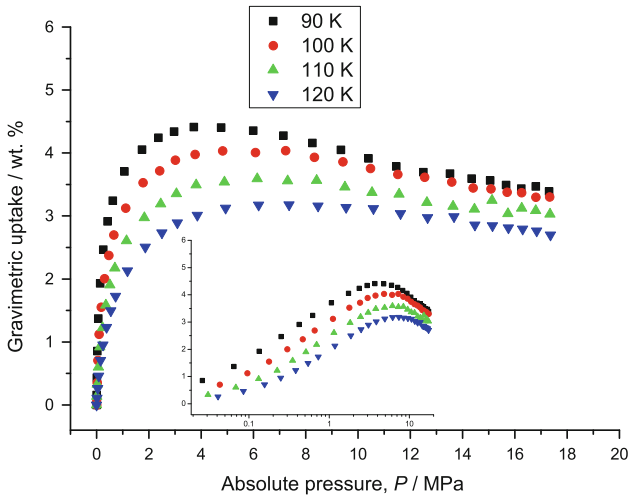

Fig. 1 Hydrogen excess isotherms for AX-21 activated carbon at 90, 100, 110 and 120 K. The *inset* plot is the same data on a logarithmic ($\log_{10}$) scale using the same units

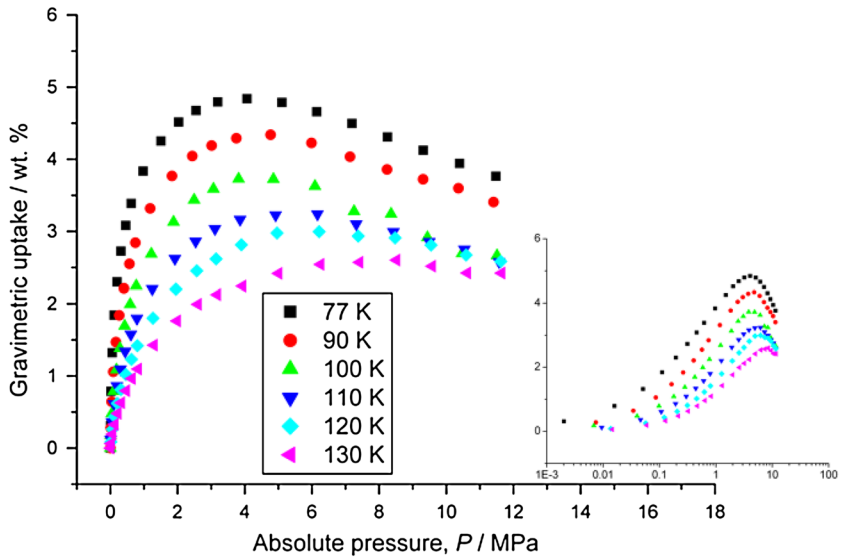

Fig. 2 Hydrogen excess isotherms for MIL-101 MOF at 77, 90, 100, 110, 120 and 130 K. The *inset* plot is the same data on a logarithmic ($\log_{10}$) scale using the same units

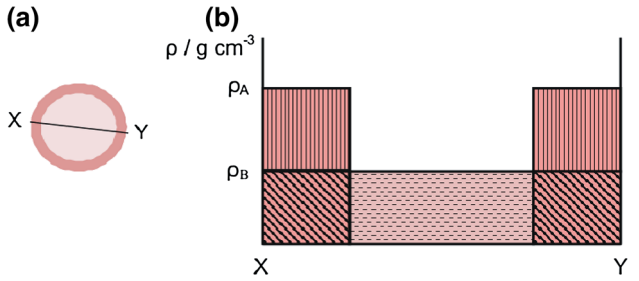

Fig. 3 The assumed hydrogen density profile within the pore, distinguishing between total, absolute and excess. **a** A cross-section of the pore. **b** The corresponding density profile, with the *x* axis representing the cross section of the pore, where ρ_A represents the mass density of the adsorbate and ρ_B represents the mass density of the bulk hydrogen. The areas correspond to the following quantities: vertical line hatching—excess; vertical and diagonal hatching—absolute; vertical, diagonal and horizontal hatching—total. Reproduced with kind permission from Springer Science+Business Media: Adsorption, Supercritical hydrogen adsorption in nanostructured solids with hydrogen density variation in pores (Sharpe et al. 2013)

type I equations in the literature that can be used to model this, including the Langmuir (1918), the Sips (1948), the UNILAN (Honig and Reyerson 1952), the Jovanović-Freundlich (Quinones and Guiochon 1996) and the Tóth equations (Toth 1971, 1962a, b, c, d, 1963a, b). The Dubinin–Astakhov (DA) (Dubinin and Astakhov 1971) and DR (Dubinin et al. 1947) can also be used as IUPAC type I equations, as shown by Richard et al. (2009). The best IUPAC type I equation to apply to experimental data is chosen depending on the observable fits, and this can be measured using statistical coefficients and by observing any bias present in the fitting.

In a recently published article, the UNILAN was considered the best equation to apply to experimental datasets of hydrogen adsorption in MOF-5 composites (Purewal et al. 2012), when compared with the Tóth and the DA. In another report, the Tóth was considered the most suited IUPAC type I equation when compared with the Sips for fitting experimental data of MOFs, zeolites and porous polymers (Tedds et al. 2011). In our work (Bimbo et al. 2011) we compared the use of the Tóth with the UNILAN, Sips, Langmuir and Jovanović-Freundlich and concluded that the Tóth provided the best fit to hydrogen excess data for the NOTT-101. Also in our previously reported work by Sharpe et al. (2013), a constant density of adsorbate was used and different equations, which included the Langmuir, Tóth, Sips, Generalised Freundlich, Jovanović-Freundlich, DA, UNILAN-Q and UNILAN-b (the UNILAN-Q is the UNILAN equation, the UNILAN-b is a development of the former presented in the paper) were tested. There were six different materials analysed, with a total of 216 fits, and the Tóth was considered the equation overall with the lowest root mean squared residual (RMSR) of all the equations tested.

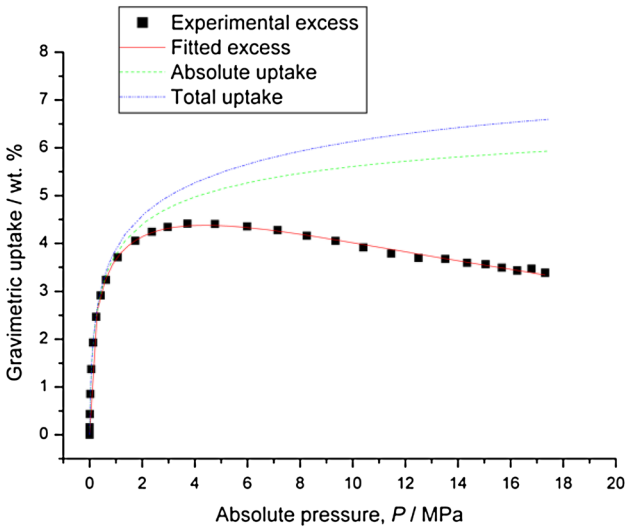

Fig. 4 Hydrogen uptake at 90 K for the AX-21 activated carbon fitted using the model that assumes a constant density of the adsorbate and distinguishes between excess, absolute and total uptake. The IUPAC type I equation used was the Tóth equation. The fitted excess is shown in the figure, along with the estimation of the absolute (*dotted line*) and total (*dash-dotted line*) uptake for this experimental dataset

The Tóth is a robust, flexible IUPAC type I equation, meaning that it converges to a statistically significant result on most datasets and can be applied to materials from MOFs to activated carbons. The Tóth is easy to use and provides meaningful and interpretable results. For this reason, the Tóth equation (4), was the equation used in the analysis presented in this work.

$$\theta_A = \frac{b_T P}{\left(1 + (b_T P)^{c_T}\right)^{\frac{1}{c_T}}} \tag{4}$$

In Eq. 4, b_T and c_T are is the affinity parameter and the heterogeneity parameter for the Tóth equation, respectively. All the hydrogen excess isotherms present in Figs. 1 and 2 for the AX-21 and the MIL-101 were fitted using Eq. 1, with the Tóth used as the IUPAC type I equation for the fractional filling. The fittings were done as previously reported (Bimbo et al. 2011, 2013; Sharpe et al. 2013) for all the temperatures and the corresponding parameters from the fit are in Supplementary Information (available online). A representative fit for the AX-21 isotherm at 90 K is shown in Fig. 4, with the excess, the fit to the experimental data and the estimated absolute and total uptake.

2.4 The different methods of calculating isosteric enthalpies

For the calculation of the enthalpies of adsorption, an important issue to consider is which H_2 quantity should be used. In the literature, the excess has often been the

quantity used for the calculation of the adsorption enthalpies. Despite some attempts to justify the use of the excess (Sircar et al. 1999) for thermodynamic calculations, this quantity is a mathematical transformation to help with the experimental measurement of adsorption, not a separate phase (Gumma and Talu 2003; Sircar 1999, 2001). The Gibbs surface excess is a concept that needs the Gibbs dividing surface and this surface has arbitrary boundaries. As the excess is a partition, it has no thermodynamic meaning as a separate phase and the isosteric enthalpies, which refer to phase changes, should be calculated using quantities that represent distinct phases.

The model that assumes a constant density for the adsorbate and distinguishes between excess, total and absolute constitutes a valid thermodynamic framework that enables discrimination of the different phases. The absolute quantity, which is the adsorbate with a constant density throughout, constitutes a clear distinct phase from the remaining bulk adsorptive in the pore and it should be the quantity to use for the calculation of the differential isosteric enthalpies of adsorption. The importance of calculating the isosteric enthalpies of adsorption using the absolute quantity has also been stressed by other authors (Mertens 2009).

The model fits an analytical equation to the excess and permits determination of both the absolute and total uptakes from experimental data, thus the adsorption enthalpies can be calculated using this thermodynamic convention (of a constant density adsorbate). The absolute uptakes are estimated and the differential isosteric enthalpies are calculated using three different methods—the virial equation, the Clausius–Clapeyron and the Clapeyron equations.

2.4.1 The Clapeyron and Clausius–Clapeyron equations

The exact thermodynamic equation for the calculation of phase change enthalpies is the Clapeyron

$$\left(\frac{\partial P}{\partial T}\right)_{n_a} = \frac{\Delta s}{\Delta v} \tag{5}$$

The Clapeyron equation relates the derivative of pressure P with respect to temperature T at constant mass amount adsorbed n_a with the change in molar entropy s over the change in molar volume v from adsorptive to adsorbate. For the calculation of enthalpies, the entropy can be expressed in terms of molar enthalpy h and temperature, so the Clapeyron equation for the calculation of differential isosteric enthalpies of adsorption at constant amount adsorbed n_a, is Eq. 6.

$$\left(\frac{\partial P}{\partial T}\right)_{n_a} = \frac{\Delta h}{T\Delta v} \tag{6}$$

Some of our previous work highlighted the differences in using the Clapeyron equation, which is the exact thermodynamic equation for phase changes with the use of the Clausius–Clapeyron equation, which is an approximation of the exact equation. The Clausius–Clapeyron equation approximates the Clapeyron equation based on two assumptions. These are that the molar volume of the bulk adsorptive is much higher than the molar volume of the adsorbate, so the molar volume of the adsorbate is ignored in calculations, and that the bulk adsorptive behaves as an ideal gas. If the molar volume of the adsorbate is ignored, the bulk gas is approximated as an ideal gas and the enthalpy of adsorption is independent of temperature (*i.e.*, the heat capacity of the adsorbed phase is zero), Eq. 6 can be integrated into:

$$\left(\frac{\partial P}{\partial T}\right)_{n_a} = \frac{\Delta h P}{RT^2} \tag{7}$$

If Eq. 7 is simplified and integrated, we get the Clausius–Clapeyron equation, where the change in enthalpy h corresponds to the differential isosteric enthalpy of adsorption Q_{st}.

$$\ln P = \frac{Q_{st}}{R}\left(\frac{1}{T_i} - \frac{1}{T_f}\right) \tag{8}$$

where i and f represent the initial and final states, inverted for the temperature difference due to the integration of $1/T^2$. As demonstrated in our earlier work (Bimbo et al. 2011), although the Clapeyron and the Clausius–Clapeyron equation converge at low pressures, with higher amounts adsorbed the enthalpies calculated using the two different methods start to diverge, since the behaviour of the adsorptive at those operating conditions is no longer ideal (hydrogen adsorption experiments are usually carried out at cryogenic temperatures and high pressures) and the molar volume of the adsorbate is no longer negligible in comparison with the molar volume of the adsorptive. For this reason, and since the isosteric enthalpy of adsorption is important for the whole range, not just at low pressures, it is important to estimate it as accurately as possible (Bhatia and Myers 2006). This is even more important when designing practical hydrogen storage systems which require accurate energy balances in their design.

2.4.2 The virial equation

Another widely used method for the enthalpies of adsorption is the virial equation, which expresses the differences to an ideal gas equation as a power series. The virial has some limitations, since convergence is only good at low pressures, with convergence at higher pressures needing many parameters (Mason and Spurling 1969). The reason why the virial equation is so widely used is that each of the virial coefficients has a definite statistical mechanics interpretation, because the second virial coefficient corresponds to deviations from ideal behaviour corresponding to interactions between two molecules, the third virial

coefficient represents deviations from ideal corresponding to interactions with three molecules and so on (Mason and Spurling 1969). For the calculation of isosteric enthalpies, the uptakes are fitted using a polynomial with an arbitrary number of parameters and the associated differential isosteric enthalpies are calculated. This method has been widely used for the calculation of the enthalpies of adsorption, especially in MOFs (Chen et al. 2008; Lin et al. 2009; Sumida et al. 2011; Zhao et al. 2005).

A common form of the virial equation is:

$$\ln\left(\frac{P}{n}\right) = \frac{1}{T}\sum_{j=0}^{l} a_j n^j + \sum_{j=0}^{m} b_j n^j \tag{9}$$

where n is the mass uptake and a and b represent the polynomial approximations. They are both described as a function of the uptake and have an adjustable number of parameters j. This form of the virial equation is based on two assumptions, described as:

$$\left[\frac{\partial \ln P}{\partial\left(1/T\right)}\right]_n = g(n) \tag{10}$$

$$\left[\frac{\partial g(n)}{\partial T}\right]_n = 0 \tag{11}$$

The adsorption isosteres are linear and $g(n)$ is a polynomial function that depends only on the amount adsorbed, *i.e.*, independent of temperature. Assuming that it agrees with Henry's law in the low coverage limit and is linear in relation to the parameters, the function $g(n)$, is then approximated as a polynomial with an adjustable number of parameters to yield the virial equation shown in Eq. 9. The numbers of parameters for the virial equation l and m are variable and can be adjusted until the statistical coefficients are satisfactory.

3 Results and analysis

3.1 The virial equation

Adsorption data for the selected materials were fitted using the virial equation shown in Eq. 9. The parameters were obtained by fitting Eq. 9 to the absolute uptakes, with the parameters shared and only T changing for the different isotherms. A systematic analysis of the different number of parameters was done, from a 2nd to a 5th order polynomial ($2 < j < 5$) and with a number of parameters in the first term always greater than in the second ($m < l$). For both materials, the number of parameters that produced the lowest χ^2_{red} was a fifth order polynomial in both terms ($l = m = 5$). The χ^2_{red} and R^2 for all the different virial fits are in Supplementary Information (available online).

The virial fits to the absolute uptake in AX-21 and MIL-101 are shown in Figs. 5 and 6 respectively.

After fitting to the data, the parameters obtained from the fitting can be used to calculate the isosteric enthalpy of adsorption, which can be calculated as a function of the uptake, as shown in Eq. 12, where R is the molar gas constant, equal to 8.314 J mol^{-1} K^{-1}.

$$Q_{st}(n) = -R\sum_{j=0}^{l} a_j n^j \tag{12}$$

3.2 The Clausius–Clapeyron and the Clapeyron equations

To calculate the isosteres, the analytical model used for the absolute uptake was solved for specific adsorbed amounts.

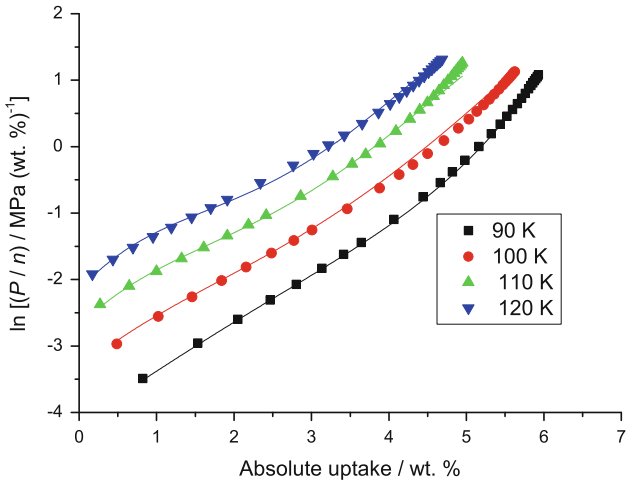

Fig. 5 Virial fits to absolute uptake of hydrogen for AX-21 activated carbon with a fifth-order polynomial on both terms

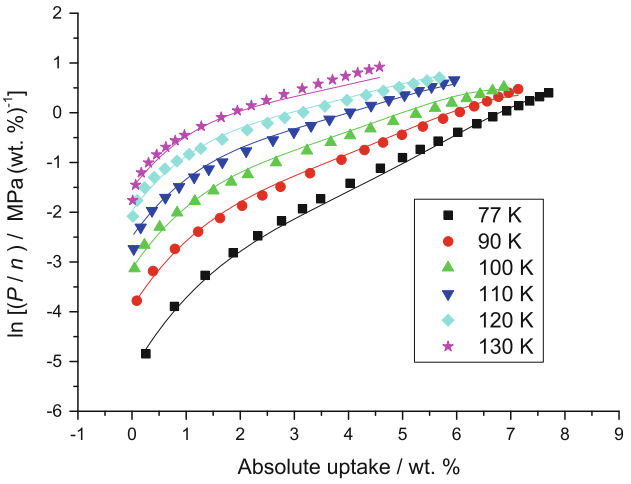

Fig. 6 Virial fits to absolute uptake of hydrogen in MIL-101 MOF with a fifth-order polynomial on both terms

For the AX-21 the chosen specific adsorbed amounts were 0.5, 1, 2, 3, 4 and 5 wt% and for MIL-101 there was an additional isostere at 6 wt%. Once the isosteres were calculated, they were plotted logarithmically against the inverse of temperature, see Eq. 8. The gradient of the curves represents the isosteric enthalpy of adsorption and it can be plotted as a function of the absolute uptake.

Figure 7 presents the isosteres and linear fits for the absolute uptakes in AX-21. It is clear from the figure that there is greater uncertainty in the linear fits with increasing amount adsorbed. This means that the isosteres are less linear the higher the loading (and the corresponding pressure), which means that some of the assumptions in the Clausius–Clapeyron might not be appropriate in these operating ranges

In Fig. 8, the isosteres and linear fits for the absolute uptakes of MIL-101 are presented. As observed for AX-21, the linear fits are worse with increasing amount adsorbed.

The coefficient of determination (R^2) is an indication of goodness of fit, with values closer to 1 indicating a better fit. In Fig. 9, the coefficient of determination for the linear fits to the isosteres in Figs. 7 and 8 is plotted for both materials. It is clear that the fits are worse with higher loadings, indicating that the Clausius–Clapeyron equation might not be the best method to estimate the isosteric enthalpies of adsorption at higher uptakes.

This difference, as indicated, is likely due to the assumptions present in the Clausius–Clapeyron equation. The assumptions are the ideal gas behaviour of the bulk adsorptive and the negligible molar volume of the

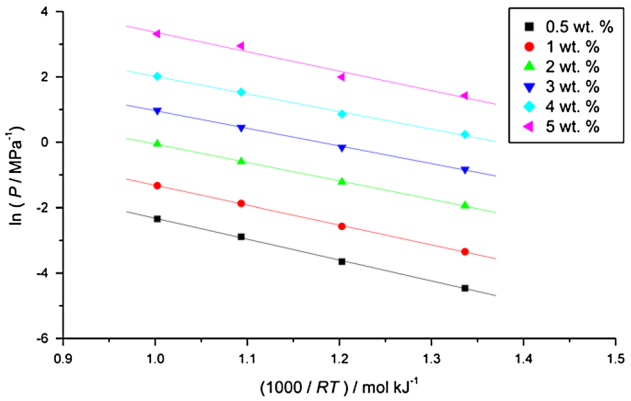

Fig. 7 The isosteres solved for 0.5, 1, 2, 3, 4 and 5 wt% calculated from the absolute uptake of hydrogen in AX-21 activated carbon. The *points* represent the isosteres and the *lines* represent the linear fits. The gradient of the linear fit is related to the isosteric enthalpy of adsorption

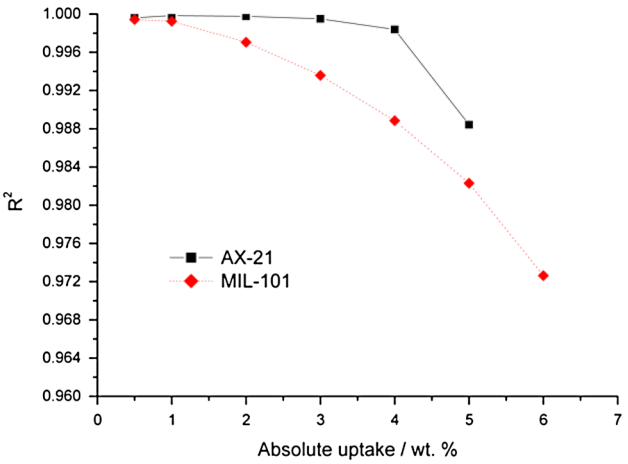

Fig. 9 The coefficient of determination for the linear fits to the hydrogen isosteres for both the AX-21 activated carbon and the MIL-101 MOF

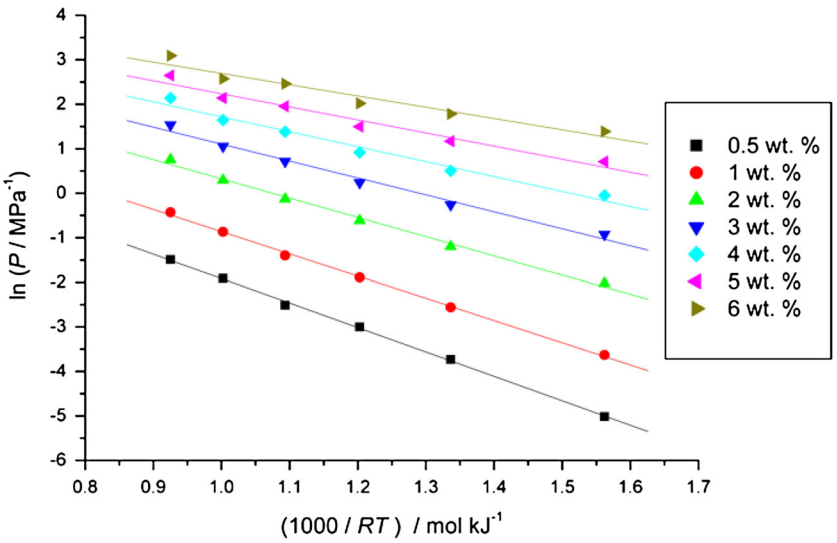

Fig. 8 The isosteres solved for 0.5, 1, 2, 3, 4, 5 and 6 wt% calculated from the absolute uptake of hydrogen in MIL-101 MOF. The *points* represent the isosteres and the *lines* represent the linear fits. The gradient of the linear fit is related to the isosteric enthalpy of adsorption

adsorbate. At the conditions of these experiments, which are temperatures between 77 and 130 K and with increasing uptakes which correspond to higher pressures, these conditions do not apply, as shown for the linear fit coefficients of determination. Since an analytical model is present for the absolute uptake, the molar volume difference can be calculated exactly from:

$$\Delta v = v_A - v_B \Leftrightarrow \frac{1}{\rho_A} - \frac{1}{\rho_B} \tag{13}$$

The adsorbate density in our model is assumed to be constant and it is one parameter that is determined from the fitting. The bulk density of hydrogen is calculated using the rational function fit to Leachman's equation of state for hydrogen (Leachman et al. 2009). The molar volume is substituted in the Clapeyron equation and the result is:

$$\left(\frac{\partial P}{\partial T}\right)_{n_a} = \frac{\Delta h}{T\left(\frac{1}{\rho_A} - \frac{1}{\rho_B}\right)} \tag{14}$$

The isosteres in the left-hand side of the equation are the same used for the Clausius–Clapeyron. Their derivative as a function of temperature is calculated using numerical differentiation. To compare with the virial equation and the Clausius–Clapeyron equation, which report the differential isosteric enthalpy as a function of the absolute uptake, the differential isosteric enthalpies were averaged for the same amount adsorbed over the different temperatures.

$$\overline{Q_{st}}(n) = \frac{1}{k}\sum_{j=1}^{k} Q_{st_j}(T_j) \tag{15}$$

3.3 Comparing the different methods

As mentioned in the introduction, for practical hydrogen storage systems it is important to calculate the differential isosteric enthalpies of adsorption as accurately as possible. The methods most commonly in use, which include the Clausius–Clapeyron and the virial equations, need to be properly evaluated and compared. The two materials chosen, the AX-21 and the MIL-101 are two high-surface area materials, the first a more structurally and chemically homogeneous material, being composed mostly of carbon atoms and possessing a narrow pore size distribution. The MIL-101 is more heterogeneous since it is made of different elements and has a tri-modal pore size distribution, with pores in the micro- and mesoporous range. To quantify the accuracy of the isosteric enthalpies, the two different equations (the virial and the Clausius–Clapeyron) were benchmarked against the values obtained with the Clapeyron equation and a RMSR was obtained for each method, with the lowest sums indicating the better approximations.

$$RMSR = \sum_{i=1}^{n} \sqrt{(x_i - y_i)^2} \tag{16}$$

In Eq. 16, the x_i and y_i indicate the isosteric enthalpies for the Clapeyron equation and the isosteric enthalpies obtained for other methods (the forms of virial and the Clausius–Clapeyron), respectively.

Figure 10 shows isosteric enthalpies of adsorption calculated using the different methods for the AX-21

The isosteric enthalpies as a function of the coverage calculated using the Clausius–Clapeyron, the Clapeyron and the virial equation with two different numbers of parameters are shown and compared. The number of parameters used for the virial are 10 ($m = 5$ and $l = 5$), which produced the best fits to isotherm data, as reflected by the lowest χ^2_{red}, and 9 ($m = 5$ and $l = 4$), which produced the lowest RMSR in comparison with the isosteric enthalpies calculated with the exact Clapeyron equation (for all the RMSR, see Supplementary Information, which is available online). Figure 10 provides some interesting features—both the Clausius–Clapeyron and the Clapeyron equation seem to converge in the low pressure range, as expected. The virial equation with 9 parameters seems to converge at low pressures with both the Clapeyron and Clausius–Clapeyron, and has a higher zero coverage value. The virial with the greater number of parameters (10 parameters) has a lower zero coverage isosteric enthalpy value which does not converge with the other values. It is also noteworthy that the virial with the most parameters and the one that fits best to isotherm data is not the one which presents the most consistent isosteric enthalpy values when compared with the Clapeyron equation. For the AX-21, the Clausius–Clapeyron equation also provided the lowest RMSR when compared with the Clapeyron equation than all the combinations of parameters of

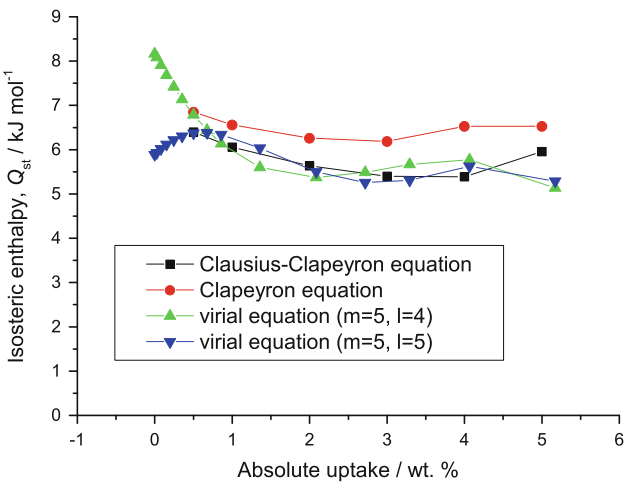

Fig. 10 The isosteric enthalpies of adsorption calculated using the virial, the Clausius–Clapeyron and the Clapeyron equation for hydrogen adsorption in AX-21 activated carbon

the virial. From Fig. 10, it is noticeable that the isosteric enthalpies do not vary much with increasing coverage (varying from $\sim$6.5 to 5.5 kJ mol^{-1}) and all the methods seem to portray these values reasonably well. It should be also be pointed out that the values are within the range of isosteric enthalpies expected for activated carbons, for example, from, direct microcalorimetric measurements of H_2 adsorption onto a range of nanoporous carbons (Matsumoto et al. 2006). Due to the relative structural and chemical homogeneity of the sample, it should not be expected that the isosteric enthalpies would change significantly with increasing uptakes.

The isosteric enthalpies of adsorption for the MIL-101 using the different methods are shown in Fig. 11. As was the case for the AX-21, the virial equation with the highest number of parameters (10, $m = 5$ and $l = 5$) provided the best fit to isotherm data, as reflected in the lowest χ^2_{red} and the virial with 9 parameters ($m = 5$ and $l = 4$) provided the most consistent isosteric enthalpies when compared with the Clapeyron equation, showing the lowest RMSR. As can be observed in Fig. 11, the isosteric enthalpies decrease much more abruptly with increasing coverage but all the different methods seem to reasonably predict this behaviour. This sharp decrease is indicative of greater structural and chemical heterogeneity, since the more energetic sites are occupied first, *i.e.,* at low coverage. Unlike the AX-21 case, the Clausius–Clapeyron equation seems to be the one that produces the least accurate results when compared with the exact Clapeyron equation. It is also interesting to note that, despite the proximity of the isosteric enthalpies, the Clapeyron equation is the one with the highest low coverage value, with a difference of $\sim$0.5 kJ mol^{-1} at 0.5 wt% for the other methods and the one with the lowest isosteric enthalpy at higher coverage,

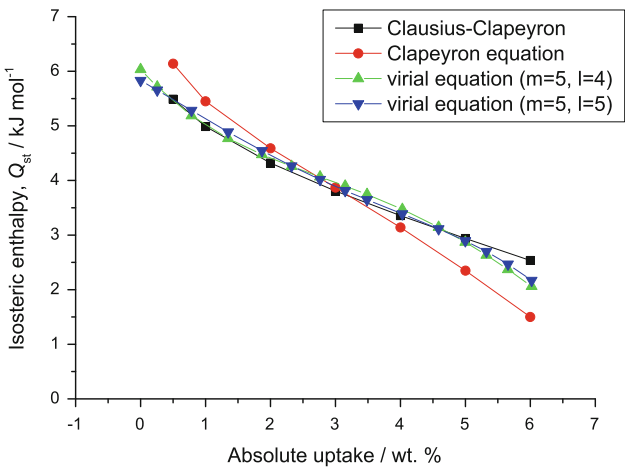

Fig. 11 The isosteric enthalpies of adsorption calculated using the virial, the Clausius–Clapeyron and the Clapeyron equation for hydrogen adsorption in MIL-101 MOF

with again a $\sim$0.5 kJ mol^{-1} difference for the virial methods at 6 wt%. It does seem that the span in isosteric enthalpies is only accurately reflected by the Clapeyron equation. Although this may not seem to be of great importance, for a hydrogen storage system containing 4 kg of hydrogen, a 0.5 kJ mol^{-1} difference in the calculation of the isosteric enthalpies represents a $\sim$1 MJ heat energy difference.

4 Conclusions

Different methods for calculating the isosteric enthalpies of adsorption were compared using experimental excess hydrogen sorption data for an activated carbon (AX-21) and a MOF (MIL-101). These are analysed in the context of hydrogen storage, since accurate calculations for the differential isosteric enthalpies of adsorption are needed, due to heat effects in practical hydrogen storage systems using nanoporous materials.

The application of a model that assumes a constant density of the adsorbate and distinguishes between the excess, absolute and total uptake is discussed. The calculations, for thermodynamic consistency, are based on the absolute uptake for the materials, as opposed to what has been calculated in the literature, which has mostly used the excess quantities. The absolute uptakes are determined from fits to experimental data and the differential isosteric enthalpies are calculated based on this quantity.

The two equations used for estimating the enthalpies of adsorption using the isosteric method—the virial and Clausius–Clapeyron equation—were compared and benchmarked against the Clapeyron equation, which is the exact thermodynamic equation for phase changes. The values resulting from the use of the virial equation were proven to be very dependent on the number of parameters used. For this reason, a systematical investigation of the use of different parameters based purely on statistical outcomes was done to assess its use. The methods were evaluated based on both the fits to data—the R^2 of the linear fits of the isosteres in the case of the Clausius–Clapeyron and both the R^2 and χ^2_{red} for the virial fits to isotherm data—and its RMSR against the isosteric enthalpies determined using the Clapeyron equation. For both materials, the virial equation that produced the best fits to isotherm data had 10 parameters ($m = 5$ and $l = 5$) but the one with the most accurate results when compared with the Clapeyron equation had 9 parameters ($m = 5$ and $l = 4$).

For the AX-21, the Clausius–Clapeyron produced more accurate results (with the lowest RMSR when compared with the results obtained by the Clapeyron equation) than any of the combinations of parameters in the virial equation. Also, the virial with 9 parameters ($m = 5$ and $l = 4$)

had a higher zero coverage value ($\sim$8 kJ mol^{-1}), which seems to be more in line with what is expected, as opposed to the lower zero coverage value presented by the virial with 10 parameters ($m = 5$ and $l = 5$) of 5.5 kJ mol^{-1}. Despite the difference of just an additional parameter, this is a substantive difference in isosteric enthalpies.

For the MIL-101, both the Clausius–Clapeyron and the two combinations of the virial (with 10 and 9 parameters) seem to predict well the isosteric enthalpies of the material over the whole coverage. However, even small inaccuracies of 0.5 kJ mol^{-1} at 0.5 and 6 wt% impact greatly on the thermal management of adsorptive hydrogen storage systems.

The need to correctly estimate enthalpies of adsorption is not exclusive for hydrogen, since adsorptive storage is being studied for other applications such as carbon dioxide capture and methane storage. The methodology described herein could be applied to other gases, and it would be interesting to observe how the isosteric enthalpies differ in other gases, such as CO_2 and CH_4.

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