

# Predicting the adsorption and isosteric heat of pure gases in active carbons with the slit-pore model, MC simulation and DFT

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## Abstract

We describe a slit-pore model and a fast density functional theory (a 'slab-DFT') that predict gas adsorption and the isosteric heat in active carbons. The DFT parameters are fitted to reproduce adsorption isotherms of each pure gas in graphitic slit pores generated by Monte-Carlo simulation. A novel feature of this work is that gas - surface interactions are calibrated to a high surface area carbon, rather than a low surface area carbon as in all previous work. We also discuss the isosteric method, correcting some errors and confusion that persist in the literature. We present predictions for the adsorption of carbon dioxide, methane, nitrogen and hydrogen up to reasonably high pressure in several active carbons at a range of temperatures based on an analysis of a single carbon dioxide adsorption isotherm. These results demonstrate that our models are accurate for relatively simple gases at near-critical or supercritical temperatures.

## Introduction

Activated carbons are used for a variety of purposes, and on an industrial scale many of them involve the separation of fluid mixtures. To design a separation process it is useful to have a phase diagram describing how fluid mixtures are adsorbed at equilibrium by a given material. However, rapid and accurate prediction of the phase behaviour of adsorbed fluid mixtures is problematic because of the number of degrees of freedom. In practice, this problem is often solved by use of a theory that predicts mixture adsorption on the basis of the adsorption of each pure component. This strategy is the basis of ideal adsorbed solution theory<sup>1</sup> (IAST). In our recent work<sup>2,3</sup> we take a further step, i.e. we predict gas mixture adsorption in active carbons given a *single* 'probe' adsorption isotherm as input. This is achieved by predicting the adsorption of each pure component from analysis of this probe isotherm, and then using a novel 'slab-DFT' to make predictions for the mixture.

Here we describe the first stage of this approach, i.e. prediction of the adsorption of pure gases up to relatively high pressure over a range of temperatures based on analysis of *one* 'probe' gas adsorption isotherm. We will describe the connection between the temperature variation of adsorption isotherms and the 'isosteric heat'<sup>4</sup>, and also present results for adsorption over a range of temperatures using our models. The second stage of our approach is dealt with in another contribution.

Our approach is based on the polydisperse independent ideal slit-pore model, Monte-Carlo simulation and a 'slab-DFT'. We use these models to predict the adsorption of carbon dioxide, methane, nitrogen and hydrogen, in several active carbons up to reasonably high pressure over a range of temperatures. The results demonstrate that these models are quite accurate for these gases at near-critical or supercritical temperatures. However, we are cautious in advocating these methods for significantly subcritical, strongly polar or complex molecular gases. Further work beyond what is presented here is needed to establish whether more detailed models are required to describe adsorption of these gases in active carbons.

A great deal of work already exists in the literature on the subject of predicting pure<sup>5-13</sup> and mixed gas<sup>14-16</sup> adsorption at a range of temperatures on the basis of a single probe gas adsorption isotherm, using either DFT or MC simulation. However, all this work, we feel, is limited because in every case gas – surface interactions are calibrated to low surface area carbons such as graphite, Sterling<sup>17</sup> or Vulcan<sup>17</sup>. The most significant contribution of our work is that it shows that much greater accuracy can be obtained if gas – surface interactions are calibrated to a reference high surface area active carbon. The premise here is that the surfaces of active carbons are more similar to each other than to low surface area carbons.

### Some thermodynamics and the isosteric method

In experiments it is excess, not absolute, quantities that are measured. Excess quantities are defined with respect to a particular pore volume,  $V_p$ , as follows

$$X^{ex} = X_a - X_b = V_p(x_a - x_b) = V_p x^{ex} \quad (1)$$

We show that a popular definition of the isosteric method in terms of a ‘differential enthalpy’<sup>18</sup> rather than ‘reversible heats’ is appropriate only when excess adsorption is calculated. When absolute adsorption is studied, as is often the case in idealised models, the isosteric method can no longer be expressed purely in terms of enthalpies, but it can still be expressed in terms of reversible heats. So expression of the isosteric method in terms of reversible heats, or the ‘isosteric heat’, is more general than in terms of enthalpies. This is important for all theoretical models of adsorption.

Active carbons have been modelled successfully as rigid adsorbent so a natural ensemble with which to study their adsorption is the grand canonical ensemble, in which we have (for a pure adsorbed fluid)

$$V_p d\omega = -SdT - Nd\mu \quad (2)$$

where  $\omega$ ,  $S$ ,  $T$ ,  $N$  and  $\mu$  are the average grand potential density, entropy, temperature, number of particles and chemical potential respectively of fluid in the pore space. The ‘isosteric heat’,  $q_{st}$ , is defined via the isosteric method<sup>18</sup>, which consists of analysing the variation of pressure with temperature at fixed adsorbed amount. Together with the above fundamental relation we write

$$q_{st} = \frac{T}{\rho_b} \left( \frac{\partial P}{\partial T} \right)_{V_p, N^{ex}} = Ts_b + T \left( \frac{\partial \mu}{\partial T} \right)_{V_p, N^{ex}} \quad (3)$$

since  $-P$  is the grand potential density and  $s_b$  is the entropy per particle of the bulk gas. Then, using (2) together with  $F = \omega V_p + \mu N$  gives

$$dF^{ex} = \omega^{ex} dV_p + \mu dN^{ex} - S^{ex} dT \quad (4)$$

from which we obtain the following Maxwell relation

$$\left(\frac{\partial\mu}{\partial T}\right)_{V_p, N^{ex}} = -\left(\frac{\partial S^{ex}}{\partial N^{ex}}\right)_{T, V_p} \quad (5)$$

It follows, at fixed grand-potential density and temperature, that

$$q_{st} = \frac{T}{\rho_b} \left(\frac{\partial P}{\partial T}\right)_{V_p, N^{ex}} = T \left(\frac{\partial S_b}{\partial N_b}\right)_{P, T} - T \left(\frac{\partial S^{ex}}{\partial N^{ex}}\right)_{T, V_p} \quad (6)$$

since entropy is extensive. The right hand expressions here are both measurements of the heat evolved when particles are reversibly added to a system under different conditions. This is why the isosteric expression (3) is called a ‘heat’. Unfortunately, whatever the experiment, the isosteric heat itself cannot ever be measured directly because it is simply not possible for  $N^{ex}$  to vary in an equilibrium system at constant  $P$ ,  $V_p$  and  $T$ . Indeed, terms of the type  $(\partial S^{ex}/\partial N^{ex})_{V_p, T, P}$ , which are sometimes seen in standard texts<sup>19</sup> and the literature<sup>20</sup>, are meaningless as they are over-constrained.

The isosteric heat is also sometimes<sup>18, 21, 22</sup> called the ‘differential enthalpy’ of adsorption because the enthalpy  $H = E + PV$ . From this definition and (1) we find

$$dH^{ex} = TdS^{ex} + \mu dN^{ex} + \omega^{ex} dV_p \quad (7)$$

and

$$\frac{H_b}{N_b} - \left(\frac{\partial H^{ex}}{\partial N^{ex}}\right)_{T, V_p} = T \left(\frac{\partial S_b}{\partial N_b}\right)_{P, T} - T \left(\frac{\partial S^{ex}}{\partial N^{ex}}\right)_{T, V_p} \quad (8)$$

which is equal to the isosteric heat. However, if absolute adsorption is employed then we have

$$q_{st} = \frac{T}{\rho_b} \left(\frac{\partial P}{\partial T}\right)_{V_p, N_a} = T \left(\frac{\partial S_b}{\partial N_b}\right)_{P, T} - T \left(\frac{\partial S_a}{\partial N_a}\right)_{T, V_p} = \frac{H_b}{N_b} - \left(\frac{\partial H_a}{\partial N_a}\right)_{T, V_p} + V_p \left(\frac{\partial P}{\partial N_a}\right)_{T, V_p} \quad (9)$$

which no longer consists purely of enthalpy terms. So we prefer expression in terms of a reversible ‘heat’ (note, this conclusion is not changed if we instead define<sup>23</sup>  $H = E - \omega V$ ).

### Pure gas adsorption prediction

In this work we employ the polydisperse independent ideal slit-pore model to model the surface of active carbons, i.e.

$$N(P) = \int_0^{\infty} dH_p f(H_p) v(H_p, P) \quad (10)$$

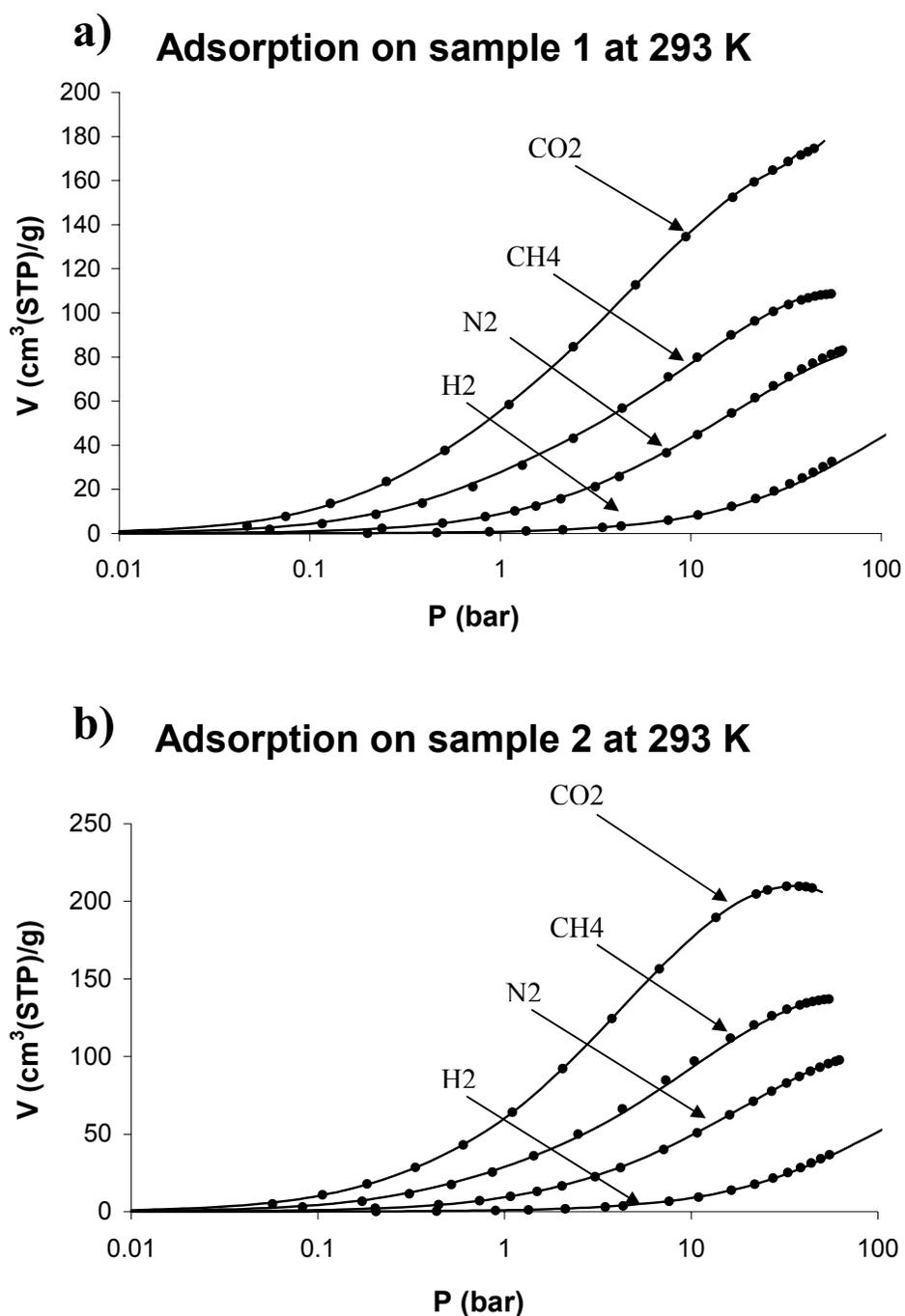
where  $f(H_p)$  is a pore-size distribution (PSD),  $H_p$  is the ‘physical’ width of a pore<sup>4</sup> and  $v(H_p, P)$  is the ‘kernel’ of ‘local’ excess isotherms. The PSD is calculated by minimising the difference, measured in terms of the root-mean-square (rms) deviation, between the

experimental probe isotherm, and the isotherm calculated from (10),  $N(P)$ , using the probe kernel. Adsorption isotherms for any gas at any temperature are then easily predicted by using the appropriate kernel with the calculated PSD.

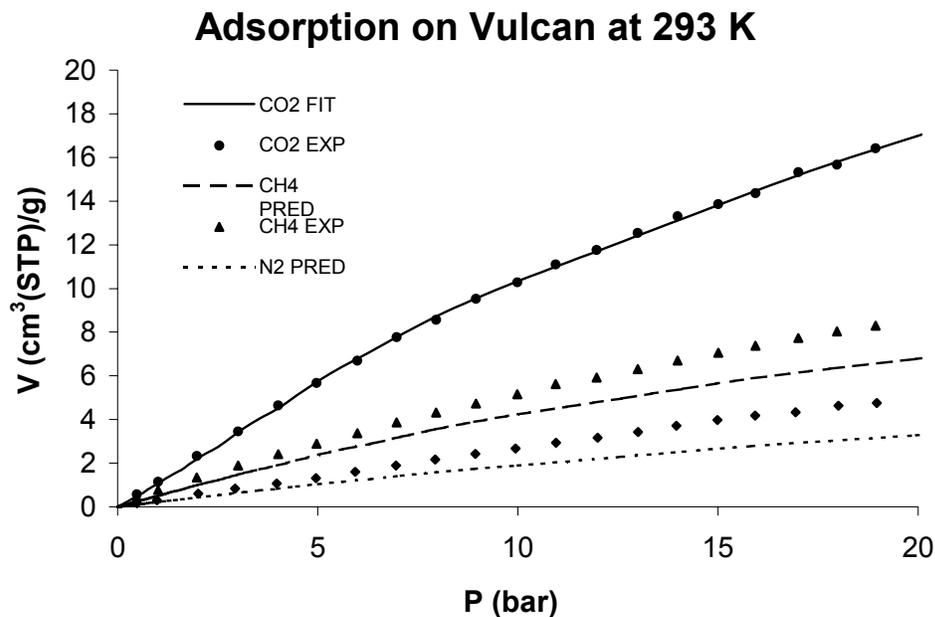
Clearly, the success of this method depends on three crucial factors; 1) the universality (in the sense that one PSD is accurate for every gas at every temperature) of the polydisperse independent ideal slit-pore model, 2) the accuracy of the solution method for obtaining the PSD, and 3) the accuracy of the kernel for each gas and temperature. A great deal of discussion in the literature has focussed on the second factor<sup>24</sup>. The third factor concerns the accuracy of a particular method for generating equilibrium isotherms for a given Hamiltonian, or molecular model. Once again, many different methods have been discussed in the literature. In this paper we employ grand-canonical Monte-Carlo simulation, which provides essentially exact results within statistical error. Since we believe our gas models to be quite accurate<sup>11</sup> this work essentially addresses the first factor, i.e. the universality of the polydisperse independent ideal slit-pore model of active carbons, the transferability of gas molecular models from bulk gas to slit pores, the Steele potential that is used to model individual pores and our method for parameterising this potential, if only for the gases and range of temperatures for which we have experimental data to make comparison. The details of this model are well documented elsewhere<sup>11</sup>.

All previous work of this type in the literature has calibrated gas – surface interactions to a low surface area carbon. This work shows that much greater accuracy can be obtained by calibrating these interactions to a high surface area carbon. Our calibration method has two steps. First, we chose the nitrogen – surface interaction to be identical to commonly used parameters for the nitrogen – graphite interaction in the literature, i.e. we choose  $\epsilon_{ww}/k_B T = 28.0$ ,  $\sigma_{ww} = 0.34$  nm and use the Lorentz-Berthelot (LB) rules to obtain cross-parameters for nitrogen – surface interactions. Then the surface – surface interaction strength,  $\epsilon_{ww}$ , for every other gas is adjusted, and the LB rules used again, to achieve the best fit to experiment for each pure gas on our reference high surface area material based on the carbon dioxide PSD. The gas molecular models for carbon dioxide, methane, nitrogen and hydrogen are tailored<sup>11</sup> to reproduce bulk properties. The kernels for these gases at 293 K are obtained by grand-canonical MC simulation<sup>11, 25</sup>.

Figure 1 shows predictions for the adsorption of these gases at 293 K on two active carbons up to reasonably high pressure using the models and methods described above. The PSD is calculated from the carbon dioxide isotherm at 293 K. The accuracy of these predictions is very satisfactory, and is similar for a wide range of active carbons that we have analysed, from ultra-high surface area carbons like AX21 to carbon molecular sieves. Figure 2 shows predictions for Vulcan (a low surface area carbon) using the same approach. These results indicate very strongly that gas-surface interactions in high surface area carbons are quite different to those in low-surface area carbons.



**Figure 1.** Adsorption isotherms of carbon dioxide, methane, nitrogen and hydrogen on active carbons. The methane, nitrogen and hydrogen isotherms (lines) are predictions based on a carbon dioxide slit-PSD and Monte-Carlo simulation kernels. Symbols are experiment. The carbon-dioxide slit-PSD is calculated from the CO<sub>2</sub> isotherm at 293 K. Gas – surface interaction strength parameters are calibrated to a reference high surface area carbon.

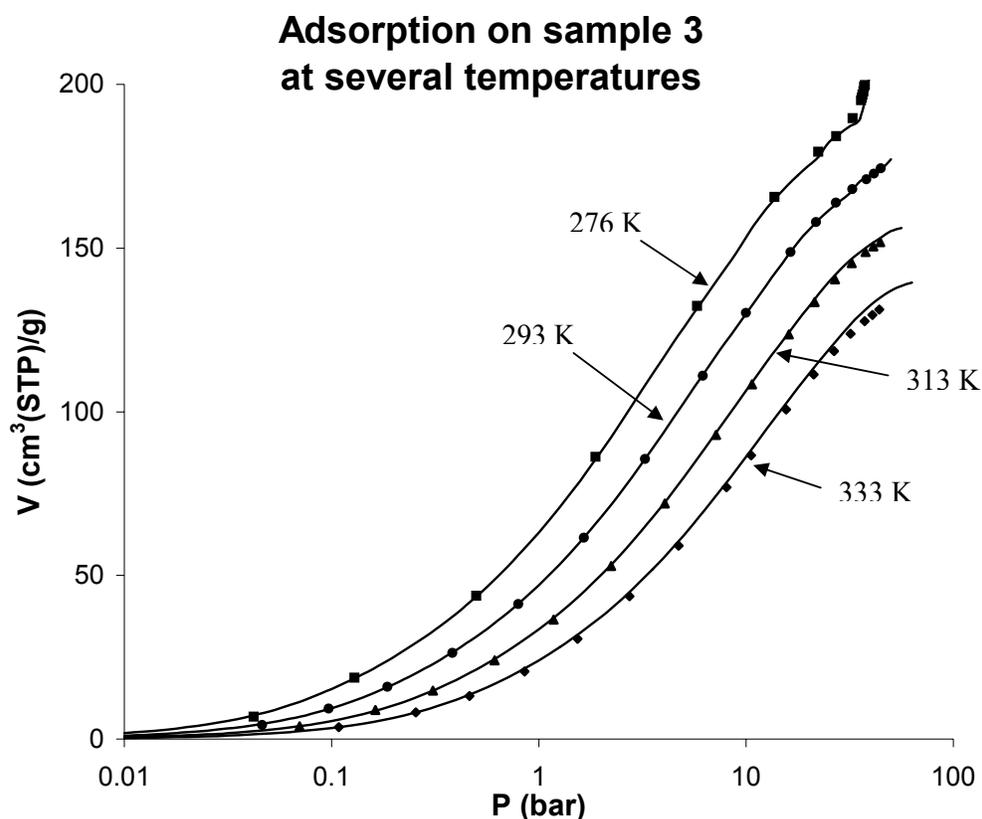


**Figure 2.** As for figure 1, except that adsorption of carbon dioxide, methane and nitrogen is shown on Vulcan, a low surface area carbon.

#### Isosteric heat prediction

According to (3) the isosteric heat can be calculated from adsorption isotherms at neighbouring temperatures. These isotherms can be predicted with the adsorption integral (10) if the relevant kernels are known. To avoid the numerical expense involved with MC simulations, we use a ‘trimmed-down’ slab-DFT<sup>26</sup> to generate these kernels. Here we examine the ability of the slab-DFT to convert a kernel at one temperature to another temperature. The slab-DFT is fully described in previous work<sup>4, 26</sup>. Essentially, it symmetrically parameterises density profiles of adsorbed fluid in slit pores in terms of five fluid slabs (a central slab flanked by two further slabs on each side). Our prescription for the excess intrinsic Helmholtz free-energy is effectively a crude non-local approximation. The DFT parameters for each pure fluid are fitted to reference (MC) isotherms for each pore width in the kernel. Then, the slab-DFT is solved for the mixture, using the LB rules to provide cross-interactions between components.

Figure 3 show predictions made with the slab-DFT for adsorption of carbon dioxide on one active carbon sample at various temperatures (the PSD is found by fitting to the 293 K isotherm). Comparison with experiment demonstrates that the slab-DFT can accurately account for changes in adsorption due to temperature changes, and therefore can be used to accurately calculate the isosteric heat.



**Figure 3.** As for figure 1, except that adsorption of carbon dioxide is shown at various temperatures on sample 3. The kernels at 276 K, 313 K and 333 K are generated by the slab-DFT, which is fitted to the 293 K MC kernel.

### Discussion

The results in Figures 1 and 3 demonstrate that the polydisperse independent ideal slit-pore model is a useful model of the surface of active carbons and is accurate for prediction of gas adsorption isotherms and isosteric heats, at least for the relatively simple gases here under the temperature and pressure ranges studied, provided that gas-surface interactions are calibrated to a high surface area carbon, rather than a low surface area carbon as in all previous work of this type. Clearly, this calibration method corrects, to some degree, for the simplicity of our surface model. Despite this success, we are cautious in recommending these models and methods to more complex systems, for example the adsorption of longer alkanes or water. Our caution results not only from the simplicity of our slab-DFT, but also from the inadequacies of our surface model. Its failure is the result of two factors; a) the modelled uniformity of individual pores, and b) the independence of these pores. In real materials there will be both geometric and energetic non-uniformities that the ideal pore model cannot capture. Indeed, it cannot even clearly distinguish energetic from geometric non-uniformity or one kind of geometry from another<sup>27-29</sup>.

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