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# Abstract

Abstract is here.

# Acknowledgements

Acknowledgements go here

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# 1 Building a framework for adsorption data processing

## 1.1 Introduction

Historically, the processing of isotherms was done by hand, with large worksheets being used for the calculations. As an example, we point out that one of the initial limitations of the BJH method was that each point had to be determined with an approximation of critical pore radius, due to the tedious work involved in the calculation.<sup>(? )</sup>

The advent of computers meant that the calculations could be performed quickly and reliably and led to the introduction of more complex methods for isotherm processing, such as the DFT method for pore size distribution.<sup>(? ? )</sup> Commercial adsorption equipment which offers the users a complete software solution for any isotherm calculations is now commonplace and makes obtaining reports of desired properties for measured materials a matter of minutes.

Given the current ubiquitousness of adsorption as a characterisation method, particularly for investigating surfaces and porous compounds, there is a large pool of data published in the scientific community. Key performance indicators such as specific surface area, working capacity and pore volume are commonly reported in scientific literature and used as benchmarking tools for comparing performance.

Recent efforts have also focused on building a database of adsorption isotherms,<sup>(? )</sup> to offer a searchable pool of standardised behaviours on different materials. This serves as both a useful reference for comparing synthesised compounds, as well as a method for quickly finding suitable materials which have the desired properties for a particular application.

In this work, we present pyGAPS, an open-source software package released under an MIT licence and written in Python, intended to be used for manipulation, storage, visualisation and processing of adsorption isotherms. Developed internally at the MADIREL Laboratory in Marseilles, the software is aimed to give users a powerful yet easy to use package that can perform the kind of processing usually offered by commercial software.

## 1.2 Methods implemented in pyGAPS

### 1.2.1 Isotherm models

#### The Henry model

Henry's law. Assumes a linear dependence of adsorbed amount with pressure.

Usually, Henry's law is unrealistic because the adsorption sites will saturate at higher pressures. Only use if your data is linear.

## BET model

The BET model assumes that adsorption happens on the surface of the material in incremental layers according to several assumptions:

- The adsorption sites are equivalent, and therefore the surface is heterogeneous
- There are no lateral interactions between adsorbed molecules
- The adsorption happens in layers, with adsorbed molecules acting as adsorption sites for new molecules
- The adsorption energy of a molecule on the second and higher layers equals the condensation energy of the adsorbent  $E_L$ .

A particular surface percentage  $\theta_x$  is occupied with x layers. For each layer at equilibrium, the adsorption and desorption rates must be equal. We can then apply the Langmuir theory for each layer.

$$k_{a1}p\theta_0 = k_{d1}\theta_1 \exp\left(-\frac{E_1}{RT}\right) \quad (1.1)$$

$$k_{a2}p\theta_1 = k_{d2}\theta_2 \exp\left(-\frac{E_L}{RT}\right) \quad (1.2)$$

$$\dots \quad (1.3)$$

$$k_{ai}p\theta_{i-1} = k_{di}\theta_i \exp\left(-\frac{E_L}{RT}\right) \quad (1.4)$$

$$(1.5)$$

Since we are assuming that all layers beside the first have the same properties, we can define  $g = \frac{k_{d2}}{k_{a2}} = \frac{k_{d3}}{k_{a3}} = \dots$ . The coverages  $\theta$  can now be expressed in terms of  $\theta_0$ .

$$\theta_1 = y\theta_0 \quad \text{where} \quad y = \frac{k_{a1}}{k_{d1}}p \exp\left(-\frac{E_1}{RT}\right) \quad (1.6)$$

$$\theta_2 = x\theta_1 \quad \text{where} \quad x = \frac{p}{g} \exp\left(-\frac{E_L}{RT}\right) \quad (1.7)$$

$$\theta_3 = x\theta_2 = x^2\theta_1 \quad (1.8)$$

$$\dots \quad (1.9)$$

$$\theta_i = x^{i-1}\theta_1 = yx^{i-1}\theta_0 \quad (1.10)$$

$$(1.11)$$

A constant C may be defined such that

$$C = \frac{y}{x} = \frac{k_{a1}}{k_{d1}}g \exp\left(\frac{E_1 - E_L}{RT}\right)\theta_i = Cx^i\theta_0 \quad (1.12)$$



For all the layers, the equations can be summed:

$$\frac{n}{n_m} = \sum_{i=1}^{\infty} i\theta^i = C \sum_{i=1}^{\infty} ix^i \theta_0 \quad (1.13)$$

Since

$$\theta_0 = 1 - \sum_1^{\infty} \theta_i \sum_{i=1}^{\infty} ix^i = \frac{x}{(1-x)^2} \quad (1.14)$$

Then we obtain the BET equation

$$L(P) = \frac{n}{n_m} = M \frac{K_A P}{(1 - K_B P)(1 - K_B P + K_A P)} \quad (1.15)$$

“Adsorption of Gases in Multimolecular Layers”, Stephen Brunauer, P. H. Emmett and Edward Teller, J. Amer. Chem. Soc., 60, 309(1938)

### Langmuir and multi-site langmuir model

The Langmuir theory, proposed at the start of the 20th century, states that adsorption happens on active sites on a surface in a single layer. It is derived based on several assumptions.

- All sites are equivalent and have the same chance of being occupied
- Each adsorbate molecule can occupy one adsorption site
- There are no interactions between adsorbed molecules
- The rates of adsorption and desorption are proportional to the number of sites currently free and currently occupied, respectively
- Adsorption is complete when all sites are filled.

Using the following assumptions we can define rates for both the adsorption and desorption. The adsorption rate will be proportional to the number of sites available on the surface, as well as the number of molecules in the gas, which is represented by the pressure. The desorption rate, on the other hand, will be proportional to the number of occupied sites and the energy of adsorption. It is also useful to define  $\theta = \frac{n_a}{M}$  as the surface coverage, the number of sites occupied divided by the total sites. Mathematically:

$$v_a = k_a p(1 - \theta) v_d = k_d \theta \exp\left(-\frac{E}{RT}\right) \quad (1.16)$$

Here,  $M$  is the moles adsorbed at the completion of the monolayer, and therefore the maximum possible loading. At equilibrium, the rate of adsorption and the rate of desorption are equal, therefore the two equations can be combined.

$$k_a p(1 - \theta) = k_d \theta \exp\left(-\frac{E}{RT}\right) \quad (1.17)$$

Rearranging to get an expression for the loading, the Langmuir equation becomes:

$$L(P) = M \frac{KP}{1 + KP} \quad (1.18)$$

The Langmuir constant is the product of the individual desorption and adsorption constants  $k_a$  and  $k_d$  and exponentially related to the energy of adsorption  $\exp\left(-\frac{E}{RT}\right)$ .

An extension to the Langmuir model is to consider the experimental isotherm to be the sum of several Langmuir-type isotherms with different monolayer capacities and affinities. The assumption is that the adsorbent presents several distinct types of homogeneous adsorption sites, and that separate Langmuir equations should be applied to each. This is particularly applicable in cases where the structure of the adsorbent suggests that different types of sites are present, such as in crystalline materials of variable chemistry like zeolites and MOFs. The resulting isotherm equation is:

$$L(P) = \sum_i M_i \frac{K_i P}{1 + K_i P} \quad (1.19)$$

In practice, up to three adsorption sites are considered. This model is the dual-site model ( $i = 2$ )

### Jensen Seaton model

When modelling adsorption in micropores, a requirement was highlighted by Jensen and Seaton in 1996, that at sufficiently high pressures the adsorption isotherm should not reach a horizontal plateau corresponding to saturation but that this asymptote should continue to rise due to the compression of the adsorbate in the pores. They came up with a semi-empirical equation to describe this phenomenon based on a function that interpolates between two asymptotes: the Henry's law asymptote at low pressure and an asymptote reflecting the compressibility of the adsorbate at high pressure.

Here  $K_H$  is the Henry constant,  $b$  is the compressibility of the adsorbed phase and  $c$  an empirical constant.

The equation can be used to model both absolute and excess adsorption as the pore volume can be incorporated into the definition of  $b$ , although this can lead to negative adsorption slopes for the compressibility asymptote. This equation has been found to provide a better fit for experimental data from microporous solids than the Langmuir or Toth equation, in particular for adsorbent/adsorbate systems with high Henry's constants where the amount adsorbed increases rapidly at relatively low pressures and then slows down dramatically.

References ——— Jensen, C. R. C.; Seaton, N. A., An Isotherm Equation for Adsorption to High Pressures in Microporous Adsorbents. *Langmuir* 1996, 12, (Copyright (C) 2012 American Chemical Society (ACS). All Rights Reserved.), 2866-2867.

## Quadratic model

The quadratic adsorption isotherm exhibits an inflection point; the loading is convex at low pressures but changes concavity as it saturates, yielding an S-shape. The S-shape can be explained by adsorbate-adsorbate attractive forces; the initial convexity is due to a cooperative effect of adsorbate-adsorbate attractions aiding in the recruitment of additional adsorbate molecules.

The parameter  $K_a$  can be interpreted as the Langmuir constant; the strength of the adsorbate-adsorbate attractive forces is embedded in  $K_b$ .

References ——— T. L. Hill, An introduction to statistical thermodynamics, Dover Publications, 1986.

## Temkin model

The Temkin adsorption isotherm, like the Langmuir model, considers a surface with  $M$  identical adsorption sites, but takes into account adsorbate-adsorbate interactions by assuming that the heat of adsorption is a linear function of the coverage. The Temkin isotherm is derived using a mean-field argument and used an asymptotic approximation to obtain an explicit equation for the loading.

Here,  $M$  and  $K$  have the same physical meaning as in the Langmuir model. The additional parameter  $\theta$  describes the strength of the adsorbate-adsorbate interactions ( $\theta < 0$  for attractions).

References ——— V. P. M.I. Tempkin, Kinetics of ammonia synthesis on promoted iron catalyst, Acta Phys. Chim. USSR 12 (1940) 327–356. Phys. Chem. Chem. Phys., 2014,16, 5499-5513

## Temkin model

The Toth model is an empirical modification to the Langmuir equation. The parameter  $t$  is a measure of the system heterogeneity.

Thanks to this addition parameter, the Toth equation can accurately describe a large number of adsorbent/adsorbate systems and is recommended as the first choice of isotherm equation for fitting isotherms of many adsorbents such as hydrocarbons, carbon oxides, hydrogen sulphide and alcohols on activated carbons but also zeolites.

## Virial model

A virial isotherm model attempts to fit the measured data to a factorized exponent relationship between loading and pressure.

$$P = n \exp (K_1 n^0 + K_2 n^1 + K_3 n^2 + K_4 n^3 + \cdots + K_i n^{i-1}) \quad (1.20)$$

It has been applied with success to describe the behaviour of standard as well as supercritical isotherms. The factors are usually empirical, although some relationship with physical can be determined: the first constant is related to the Henry constant at

zero loading, while the second constant is a measure of the interaction strength with the surface.

$$K_1 = -\ln K_{H,0} \quad (1.21)$$

In practice, besides the first constant, only 2-3 factors are used.

### Vacancy solution theory models

As a part of the Vacancy Solution Theory (VST) family of models, it is based on concept of a “vacancy” species, denoted  $v$ , and assumes that the system consists of a mixture of these vacancies and the adsorbate.

The VST model is defined as follows:

- A vacancy is an imaginary entity defined as a vacuum space which acts as the solvent in both the gas and adsorbed phases.
- The properties of the adsorbed phase are defined as excess properties in relation to a dividing surface.
- The entire system including the adsorbent are in thermal equilibrium however only the gas and adsorbed phases are in thermodynamic equilibrium.
- The equilibrium of the system is maintained by the spreading pressure which arises from a potential field at the surface

It is possible to derive expressions for the vacancy chemical potential in both the adsorbed phase and the gas phase, which when equated give the following equation of state for the adsorbed phase:

$$\pi = -\frac{R_g T}{\sigma_v} \ln y_v x_v \quad (1.22)$$

where  $y_v$  is the activity coefficient and  $x_v$  is the mole fraction of the vacancy in the adsorbed phase. This can then be introduced into the Gibbs equation to give a general isotherm equation for the Vacancy Solution Theory where  $K_H$  is the Henry’s constant and  $f(\theta)$  is a function that describes the non-ideality of the system based on activity coefficients:

$$P = \frac{n_{ads}}{K_H} \frac{\theta}{1 - \theta} f(\theta) \quad (1.23)$$

The general VST equation requires an expression for the activity coefficients. The Wilson equation can be used, which expresses the activity coefficient in terms of the mole fractions of the two species (adsorbate and vacancy) and two constants  $\Lambda_{1v}$  and  $\Lambda_{1v}$ . The equation becomes:

$$P = \left( \frac{n_{ads}}{K_H} \frac{\theta}{1-\theta} \right) \left( \Lambda_{1v} \frac{1 - (1 - \Lambda_{v1})\theta}{\Lambda_{1v} + (1 - \Lambda_{1v})\theta} \right) \exp \left( - \frac{\Lambda_{v1}(1 - \Lambda_{v1})\theta}{1 - (1 - \Lambda_{v1})\theta} - \frac{(1 - \Lambda_{1v})\theta}{\Lambda_{1v} + (1 - \Lambda_{1v})\theta} \right) \quad (1.24)$$

Cochran developed a simpler, three parameter equation based on the Flory-Huggins equation for the activity coefficient. The equation for then becomes:

$$P = \left( \frac{n_{ads}}{K_H} \frac{\theta}{1-\theta} \right) \exp \frac{\alpha_{1v}^2 \theta}{1 + \alpha_{1v} \theta} \alpha_{1v} = \frac{\alpha_1}{\alpha_v} - 1 \quad (1.25)$$

where  $\alpha_1$  and  $\alpha_v$  are the molar areas of the adsorbate and the vacancy respectively.

References ——— Cochran, T. W.; Kabel, R. L.; Danner, R. P., Vacancy solution theory of adsorption using Flory-Huggins activity coefficient equations. *AIChE J.* 1985, 31, 268-77.

Suwanayuen, S.; Danner, R. P., Gas-Adsorption Isotherm Equation Based On Vacancy Solution Theory. *AIChE Journal* 1980, 26, (1), 68-76.

## 1.2.2 Thickness functions

## 1.2.3 BET surface area

The BET surface area is one of the first standardised methods to calculate the surface area of a porous material. It is generally applied on isotherms obtained through N2 adsorption at 77K, although other adsorbates (Ar, Kr) have been used.

It assumes that the adsorption happens on the surface of the material in incremental layers according to the BET theory. Even if the adsorbent is porous, the initial amount adsorbed (usually between 0.05 - 0.4  $p/p_0$ ) can be modelled through the BET equation:

$$\frac{p/p_0}{n_{ads}(1 - p/p_0)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} (p/p_0) \quad (1.26)$$

Therefore, if we plot the isotherm points as  $\frac{p/p_0}{n_{ads}(1 - p/p_0)}$  versus  $p/p_0$ , a linear region can usually be found. The slope and intercept of this line can then be used to calculate  $n_m$ , the amount adsorbed at the statistical monolayer, as well as C, the BET constant.

$$n_m = \frac{1}{s + i} C = \frac{s}{i} + 1 \quad (1.27)$$

The surface area can then be calculated by using the moles adsorbed at the statistical monolayer. If the specific area taken by one of the adsorbate molecules on the surface is known, it is inserted in the following equation together with Avogadro's number:

$$a(BET) = n_m A_N \sigma \quad (1.28)$$

*Limitations*

While a standard for surface area determinations, the BET area should be used with care, as there are many assumptions made in the calculation. To augment the validity of the BET method, Rouquerol<sup>(?)</sup> proposed several checks to ensure that the BET region selected is valid:

- The BET constant (C) obtained should be positive
- In the corresponding Rouquerol plot where  $n_{ads}(1 - p/p_0)$  is plotted with respect to  $p/p_0$ , the points chosen for BET analysis should be strictly increasing
- The loading at the statistical monolayer should be situated within the limits of the BET region

This module implements all these checks.

Regardless, the BET surface area should still be interpreted carefully. The following assumptions are implicitly made in this approach:

- Adsorption takes place on the pore surface. Microporous materials which have pores in similar size as the molecule adsorbed cannot have a realistic surface area
- The cross-sectional area of the molecule on the surface cannot be guaranteed. For example, nitrogen has been known to adopt a different conformation on the surface of some materials, due to inter-molecular forces, which effectively lowers its cross-sectional area.
- No account is made for adsorbate-adsorbent interaction in BET theory

#### References

“Adsorption of Gases in Multimolecular Layers”, Stephen Brunauer, P. H. Emmett and Edward Teller, J. Amer. Chem. Soc., 60, 309(1938)

### 1.2.4 Langmuir surface area

The Langmuir theory, proposed at the start of the 20th century, states that adsorption happens on active sites on a surface in a single layer. It is derived based on several assumptions.

- All sites are equivalent and have the same chance of being occupied
- Each adsorbate molecule can occupy one adsorption site
- There are no interactions between adsorbed molecules
- The rates of adsorption and desorption are proportional to the number of sites currently free and currently occupied, respectively
- Adsorption is complete when all sites are filled.

The Langmuir equation is then:

$$n = n_m \frac{KP}{1 + KP} \quad (1.29)$$

The equation can be rearranged as:

$$\frac{P}{n} = \frac{1}{Kn_m} + \frac{P}{n_m} \quad (1.30)$$

Assuming the data can be fitted with a Langmuir model, by plotting  $\frac{P}{n}$  against pressure, a line will be obtained. The slope and intercept of this line can then be used to calculate  $n_m$ , the amount adsorbed at the monolayer, as well as  $K$ , the Langmuir constant.

$$n_m = \frac{1}{s}K = \frac{1}{i * n_m} \quad (1.31)$$

The surface area can then be calculated by using the moles adsorbed at the monolayer. If the specific area taken by one of the adsorbate molecules on the surface is known, it is inserted in the following equation together with Avogadro's number:

$$a(Langmuir) = n_m A_N \sigma \quad (1.32)$$

#### Limitations

The Langmuir method for determining surface area assumes that only one single layer is adsorbed on the surface of the material. As most adsorption processes (except chemisorption) don't follow this behaviour, it is important to regard the Langmuir surface area as an estimate.

#### References

I. Langmuir, J. American Chemical Society 38, 2219(1916); 40, 1368(1918)

### 1.2.5 t-plot Method

The t-plot method attempts to relate the adsorption on a material with an ideal curve which describes the thickness of the adsorbed layer on a surface. A plot is constructed, with the isotherm loading data is plotted versus thickness values obtained through the model. It stands to reason that, in the case that the experimental adsorption curve follows the model, a straight line will be obtained with its intercept through the origin. However, since in most cases there are differences between adsorption in the pores and ideal surface adsorption, the t-plot will deviate and form features which can be analysed to describe the material characteristics.

- a sharp vertical deviation will indicate condensation in a type of pore
- a gradual slope will indicate adsorption on the wall of a particular pore

The slope of the linear section can be used to calculate the area where the adsorption is taking place. If it is of a linear region at the start of the curve, it will represent the total surface area of the material. If at the end of the curve, it will instead represent external surface area of the sample. The formula to calculate the area is where  $\rho_l$  is the liquid density of the adsorbate at experimental conditions

$$A = \frac{sM_m}{\rho_l} \quad (1.33)$$

If the region selected is after a vertical deviation, the intercept of the line will no longer pass through the origin. This intercept be used to calculate the pore volume through the following equation:

$$V_{ads} = \frac{iM_m}{\rho_l} \quad (1.34)$$

Since the t-plot method is taking the differences between the isotherm and a model, care must be taken to ensure that the model actually describes the thickness of a layer of adsorbate on the surface of the adsorbent. This is more difficult than it appears as no universal thickness curve exists. When selecting a thickness model, make sure that it is applicable to both the material and the adsorbate. Interactions at loadings that occur on the t-plot lower than the monolayer thickness do not have any physical meaning.

“Studies on Pore Systems in Catalysts V. The t Method”, B. C. Lippens and J. H. de Boer, J. Catalysis, 4, 319 (1965)

### 1.2.6 $\alpha_s$ Method

In order to extend the t-plot analysis with other adsorbents and non-standard thickness curves, the  $\alpha_s$  method was devised. Instead of a formula that describes the thickness of the adsorbed layer, a reference isotherm is used. This isotherm is measured on a non-porous version of the material with the same surface characteristics and with the same adsorbate. The  $\alpha_s$  values are obtained from this isotherm by regularisation with an adsorption amount at a specific relative pressure, usually taken as 0.4 since nitrogen hysteresis loops theoretically close at this value.

$$\alpha_s = \frac{n_a}{n_{0.4}} \quad (1.35)$$

The analysis then proceeds as in the t-plot method.

The slope of the linear section can be used to calculate the area where the adsorption is taking place. If it is of a linear region at the start of the curve, it will represent the total surface area of the material. If at the end of the curve, it will instead represent external surface area of the sample. The calculation uses the known area of the reference material. If unknown, the area will be calculated here using the BET method.

$$A = \frac{sA_{ref}}{(n_{ref})_{0.4}} \quad (1.36)$$



If the region selected is after a vertical deviation, the intercept of the line will no longer pass through the origin. This intercept be used to calculate the pore volume through the following equation:

$$V_{ads} = \frac{iM_m}{\rho_l} \quad (1.37)$$

The reference isotherm chosen for the  $\alpha_s$  method must be a description of the adsorption on a completely non-porous sample of the same material. It is often impossible to obtain such non-porous versions, therefore care must be taken how the reference isotherm is defined.

D. Atkinson, A.I. McLeod, K.S.W. Sing, J. Chim. Phys., 81, 791 (1984)

### 1.2.7 Isotheric heat

The isotheric heats are calculated from experimental data using the Clausius-Clapeyron equation as the starting point:

$$\left( \frac{\partial \ln P}{\partial T} \right)_{n_a} = - \frac{\Delta H_{ads}}{RT^2} \quad (1.38)$$

Where  $\Delta H_{ads}$  is the enthalpy of adsorption. In order to approximate the partial differential, two or more isotherms are measured at different temperatures. The assumption made is that the heat of adsorption does not vary in the temperature range chosen. Therefore, the isotheric heat of adsorption can be calculated by using the pressures at which the loading is identical using the following equation for each point:

$$\Delta H_{ads} = -R \frac{\partial \ln P}{\partial 1/T} \quad (1.39)$$

and plotting the values of  $\ln P$  against  $1/T$  we should obtain a straight line with a slope of  $-\Delta H_{ads}/R$ .

\*Limitations\*

The isotheric heat is sensitive to the differences in pressure between the two isotherms. If the isotherms measured are too close together, the error margin will increase.

The method also assumes that enthalpy of adsorption does not vary with temperature. If the variation is large for the system in question, the isotheric heat calculation will give unrealistic values.

Even with carefully measured experimental data, there are two assumptions used in deriving the Clausius-Clapeyron equation: an ideal bulk gas phase and a negligible adsorbed phase molar volume. These have a significant effect on the calculated isotheric heats of adsorption, especially at high relative pressures and for heavy adsorbates.

### 1.2.8 Kelvin model

The standard kelvin equation for determining critical pore radius for condensation or evaporation.

**\*Limitations\***

The Kelvin equation assumes that adsorption in a pore is not different than adsorption on a standard surface. Therefore, no interactions with the adsorbent is accounted for.

Furthermore, the geometry of the pore itself is considered to be invariant across the entire adsorbate.

Calculates the pore size distribution using a 'classical' model which attempts to describe the adsorption in a pore as a combination of a statistical thickness and a condensation/evaporation behaviour described by surface tension

Currently, the methods provided are:

- the BJH or Barrett, Joyner and Halenda method - the DH or Dollimore-Heal method, an extension of the BJH method

A common mantra of data processing is: "garbage in = garbage out". Only use methods when you are aware of their limitations and shortcomings.

According to Rouquerol, in adopting this approach, it is assumed that:

- The Kelvin equation is applicable over the pore range (mesopores). Therefore in pores which are below a certain size (around 2.5 nm), the granularity of the liquid-vapour interface becomes too large for classical bulk methods to be applied. - The meniscus curvature is controlled by the pore size and shape. Ideal shapes for the curvature are assumed. - The pores are rigid and of well defined shape. They are considered open-ended and non-intersecting - The filling/emptying of each pore does not depend on its location. - The adsorption on the pore walls is not different from surface adsorption.

## 1.2.9 Mesoporous size distribution

The BJH or Barrett, Joyner and Halenda method for calculation of pore size distribution is based on a classical description of the adsorbate behaviour in the adsorbent pores. Under this method, the adsorbate is adsorbing on the pore walls in a predictable way, and decreasing the apparent pore volume until condensation takes place, filling the entire pore. The two variables, layer thickness and radius where condensation takes place can be modelled by a thickness model (such as Halsey, Harkins & Jura, etc.) and a critical radius model for condensation/evaporation, based on a form of the Kelvin equation.

$$r_p = t + r_k \quad (1.40)$$

The original model used the desorption curve as a basis for calculating pore size distribution. Between two points of the curve, the volume desorbed can be described as the volume contribution from pore evaporation and the volume from layer thickness decrease as per the equation above. The computation is done cumulatively, starting from the filled pores and calculating for each point the volume adsorbed in a pore from the following equation:

$$V_p = \left( \frac{\bar{r}_p}{\bar{r}_k + \Delta t_n} \right)^2 \quad (1.41)$$

$$(\Delta V_n - \Delta t_n \sum_{i=1}^{n-1} \Delta A_p) \quad (1.42)$$

$$+ \Delta t_n \bar{t}_n \sum_{i=1}^{n-1} \frac{\Delta A_p}{\bar{r}_p} A = 2\Delta V_p / r_p \quad (1.43)$$

Where:

- $\Delta A_p$  is the area of the pores
- $\Delta V_p$  is the adsorbed volume change between two points
- $\bar{r}_p$  is the average pore radius calculated as a sum of the kelvin radius and layer thickness of the pores at pressure p between two measurement points
- $\bar{r}_k$  is the average kelvin radius between two measurement points
- $\bar{t}_n$  is the average layer thickness between two measurement points
- $\Delta t_n$  is the average change in layer thickness between two measurement points

Then, by plotting  $\Delta V / (2 * \Delta r_p)$  versus the width of the pores calculated for each point, the pore size distribution can be obtained.

"The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms", Elliott P. Barrett, Leslie G. Joyner and Paul P. Halenda, J. Amer. Chem. Soc., 73, 373 (1951)

"Adsorption by Powders & Porous Solids", F. Roquerol, J Roquerol and K. Sing, Academic Press, 1999

### 1.2.10 Microporous size distribution

The H-K method attempts to describe the adsorption within pores by calculation of the average potential energy for a pore. The method starts by assuming the relationship between the gas phase as being:

$$R_g T \ln\left(\frac{p}{p_0}\right) = U_0 + P_a \quad (1.44)$$

Here  $U_0$  is the potential function describing the surface to adsorbent interactions and  $P_a$  is the potential function describing the adsorbate- adsorbate interactions. This equation is derived from the equation of the free energy of adsorption at constant temperature where term  $T\Delta S^{tr}(w/w_\infty)$  is assumed to be negligible.

If a Lennard-Jones-type potential function describes the interactions between the adsorbate molecules and the adsorbent molecules then the two contributions to the total potential can be replaced by the extended function. The resulting equation becomes:

$$RT \ln(p/p_0) = N_A \frac{n_a A_a + n_A A_A}{2\sigma^4(l-d)} \quad (1.45)$$

$$\times \int_{d/2}^{1-d/2} \left[ -\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{l-r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^4 \right] dx \quad (1.46)$$

Where:

- $R$  – gas constant
- $T$  – temperature
- $l$  – width of pore
- $d$  – defined as  $d = d_a + d_A$  the sum of the diameters of the adsorbate and adsorbent molecules
- $N_A$  – Avogadro's number
- $n_a$  – number of molecules of adsorbent
- $A_a$  – the Lennard-Jones potential constant of the adsorbent molecule defined as

$$A_a = \frac{6mc^2\alpha_a\alpha_A}{\alpha_a/\chi_a + \alpha_A/\chi_A} \quad (1.47)$$

- $A_A$  – the Lennard-Jones potential constant of the adsorbate molecule defined as

$$A_a = \frac{3mc^2\alpha_A\chi_A}{2} \quad (1.48)$$

- $m$  – mass of an electron
- $c$  – speed of light in vacuum
- $\alpha_a$  – polarizability of the adsorbate molecule
- $\alpha_A$  – polarizability of the adsorbent molecule
- $\chi_a$  – magnetic susceptibility of the adsorbate molecule
- $\chi_A$  – magnetic susceptibility of the adsorbent molecule

**\*Limitations\***

The assumptions made by using the H-K method are:

- It does not have a description of capillary condensation. This means that the pore size distribution can only be considered accurate up to a maximum of 5 nm.
- Each pore is uniform and of infinite length. Materials with varying pore shapes or highly interconnected networks may not give realistic results.
- The wall is made up of single layer atoms. Furthermore, since the HK method is reliant on knowing the properties of the surface atoms as well as the adsorbent molecules the material should ideally be homogenous.
- Only dispersive forces are accounted for. If the adsorbate-adsorbent interactions have other contributions, the Lennard-Jones potential function will not be an accurate description of pore environment.

References ——— K. Kutics, G. Horvath, Determination of Pore size distribution in MSC from Carbon-dioxide Adsorption Isotherms, 86

### 1.2.11 Multiscale size distribution - DFT fitting

The function will take the data in the form of pressure and loading. It will then load the kernel either from disk or from memory and define a minimization function as the sum of squared differences of the sum of all individual kernel isotherm loadings multiplied by their contribution as per the following function:

$$f(x) = \sum_{p=p_0}^{p=p_x} (n_{p,exp} - \sum_{w=w_0}^{w=w_y} n_{p,kernel} X_w)^2 \quad (1.49)$$

## 1.3 Method

### 1.3.1 Intended use cases

The software was imagined for use in two types of scenario. First, as a command line interface, in environments such as IPython and Jupyter. The typical user working in these environments is likely to be processing a small batch of results at one time, and is interested in obtaining the results in graphical form. For this type of application, the framework should provide an unobtrusive way of importing the user data, as well as present an API which does not require extensive knowledge of processing methods. Finally, a powerful graphing environment is required which will allow the user to visualise their original dataset and results.

The second envisaged application is related to bulk data processing. Requirements here shift towards parameter control, scripting and extensibility. The framework API should offer the option to change implicit parameters, select calculation limits and return

the results in a numerical form for further processing. This type of application is also likely to require storage of isotherms in a database or under other types of data files.

### 1.3.2 Core structure

In order to offer a clear structuring of functionality, **pyGAPS** introduces several classes which abstract data and functionality for facile interaction. The classes are intuitively named: **Isotherm**, **Sample** and **Adsorbent**.

The **Isotherm** class is a representation of an adsorption isotherm i.e. a function of the amount adsorbed, or loading, with pressure at a fixed temperature. The class also contains other information relating to the isotherm, such as the material name and batch it describes, the adsorbate used and other user-defined properties.

Because the aforementioned relationship can be either a physical measurement defined by individual pressure-loading pairs or a model, describing the relationship as a function rather than discrete data, the **Isotherm** class is used as a parent class for two subclasses: **PointIsotherm**, describing datapoints and **ModelIsotherm** containing a model such as Henry, Langmuir etc., which encapsulate the respective functionality. The two classes are interchangeable as they share most methods and properties. Once an instance of an **Isotherm** class is created, it can then be used for the processing, conversion and graphing capabilities of **pyGAPS**.

The isotherm classes contain the name and batch of the sample they are measured on in a string format. The user might want to specify other information about the material, such as the date of synthesis or the material's density, as well as store this information in the database. For this case, **pyGAPS** provides the **Sample** class. The framework uses the string values in the isotherm to connect an **Isotherm** instance to a specific **Sample**.

Finally, in order for many of the calculations included in **pyGAPS** to be performed, properties of the adsorbate used are needed e.g. liquid density, vapour pressure etc. The **Adsorbate** class is provided for this purpose, which is connected to an **Isotherm** class similarly to a **Sample**. The physical properties are either calculated in the background through an equation of state, either the open source CoolProp library<sup>(?)</sup> or the NIST-made REFPROP.<sup>(?)</sup> The properties can also be retrieved from the internal database or specified by the user.

### 1.3.3 Creation of an Isotherm

An **Isotherm** can be created either from the command line directly or through an import from a supported format. For the direct creation, the code takes two kinds of inputs: the data itself, in the form of a **pandas.DataFrame**, and the isotherm parameters describing it. Only four parameters are strictly required: the material name, the material batch, the adsorbate used and the experimental temperature. Other parameters can be passed as well and will be stored in the isotherm class.

The **DataFrame** must contain a column containing the pressure points and one containing the corresponding loading points of the isotherm. Other columns can also be

passed, when secondary data such as enthalpy of adsorption is present at each measurement point. These columns will be saved in the case of the `PointIsotherm` class and can be plotted afterwards.

If no unit data is specified in the constructor, the framework will assume that the isotherm is in units of  $\text{mmol g}^{-1}$  loading as a function of bar. Both the units and the basis can be specified, as it is explained in a latter section.

Finally, the data is saved in the newly created class or used to generate parameters for a model such as BET, Langmuir, etc., in the case of a `PointIsotherm` and `ModelIsotherm` respectively. It should be noted that the creation of `Sample` and `Adsorbate` instances is similar.

Alternatively, the isotherm can be imported from a file containing a format that is recognised by `pyGAPS`. Parsing from suitably structured JSON, CSV and Excel files is supported.

### 1.3.4 Workflow

Once an isotherm object is created, it will be used for all further processing. The class contains methods which can be used to inspect the data visually, or retrieve parts of the isotherm such as the adsorption or desorption branches with user-chosen limits or units. Singular values of pressure or loading can be calculated, either through interpolation in the case of a `PointIsotherm` or by evaluation of the internal model in the `ModelIsotherm`. For an isotherm with datapoints, these can also be converted into different units or modes.

Characterisation functions take a single isotherm object as their first parameter. This is the case for the BET area, Langmuir area, t-plot,  $\alpha_s$  plot, and pore size distribution methods. These characterisation functions attempt to automate as much of the process as possible. For example, the BET area limits are automatically calculated using the Rouquerol<sup>(?)</sup> method, with all the checks implemented into the code. In another example the straight line sections of the t-plot are determined automatically through a calculation of the second derivative of the transformed isotherm. For detailed control, there is an option to specify options for each individual method, such as manual BET limits, different thickness functions for the t-plot or Kelvin-based mesoporous pore distribution methods, custom parameters for the Horvath-Kawazoe microporous pore distribution, custom DFT or NLDFIT kernels and more. The results are returned in a dictionary or can be directly graphed if the `verbose` parameter is passed.

### 1.3.5 Units

When computers work with physical data, units are often a matter that introduces confusion. Here we explain how `pyGAPS` handles units and other physical world concepts such as relative pressure and mass or volume basis.

The following dimensions can be specified for an Isotherm: the measurement *pressure*, the quantity of guest adsorbed or *loading* and the amount of adsorbent material the loading is reported on, or *adsorbent*.

Pressure can be reported either in an absolute value, in several common units such as bar, torr, Pa, or as *relative pressure*, the pressure divided by the saturation vapour pressure of the adsorbate at the respective measurement temperature. Conversions between the two modes are automatic and handled internally.

Both the *loading* and *adsorbent* can be reported in three different bases: a molar basis, a mass basis or a volume basis. Within each basis different units are recognised and can be easily converted. The conversions between bases can also easily performed if the required conversion factors (i.e. molar mass and density) are available. For *loading*, these factors are automatically calculated internally, while for the *adsorbent* they should be provided by the user in the respective `Sample` class.

## 1.4 Case studies

### 1.4.1 Routine characterization of a MOF sample

The UiO-66(Zr) MOF and its derivatives are well known due to their thermal and chemical stability.<sup>(?)</sup> It is composed of  $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$  clusters which are connected with benzene dicarboxylate (BDC) linkers to form a face-centered cubic framework. It has shown promise<sup>(?)</sup> in use for gas adsorption and catalytic applications.

When a newly synthesised sample is available, an initial characterisation is often performed to compare the material with previous batches. Adsorption of nitrogen at 77 K is commonly used to verify if predictors such as specific surface area and pore size distribution are consistent with other samples or literature values.

The nitrogen isotherm is first imported in `pyGAPS`. To obtain the BET area, the `pygaps.area_BET()` method is used with the isotherm object as the parameter and the verbose option, with Figure 1.1 as the output. It can be seen that the framework has automatically selected the points within the applicable BET region using the checks devised by Rouquerol et al.<sup>(?)</sup> to assert method validity. The statistical BET monolayer point is within the selected region, which is one of the checks implemented for method validity. The calculated surface area is  $1277 \text{ m}^2/\text{g}$ , which is similar to literature values.<sup>(? ?)</sup>

The same isotherm is used to calculate the pore size distribution of the UiO-66(Zr) sample. This MOF has octahedral cages surrounded by eight corner tetrahedral cages of 11 and 8 Å respectively. The structure is therefore expected to have only micropores. Two methods are available in `pyGAPS` for micropore size distributions: a ‘classical’ Horvath-Kawazoe (HK) method,<sup>(?)</sup> as well as a DFT fitting routine. The HK method is called by using the function in Listing 1.1. Here, the surface characteristic parameters determined by Saito and Foley<sup>(?)</sup> are to be used, with the framework automatically supplying the parameters for the adsorbed gas.

Listing 1.1: Calculating the PSD

```
pygaps.micropore_size_distribution(iso,
                                   psd_model='HK',
                                   adsorbent_model='OxideIon(SF)')
```



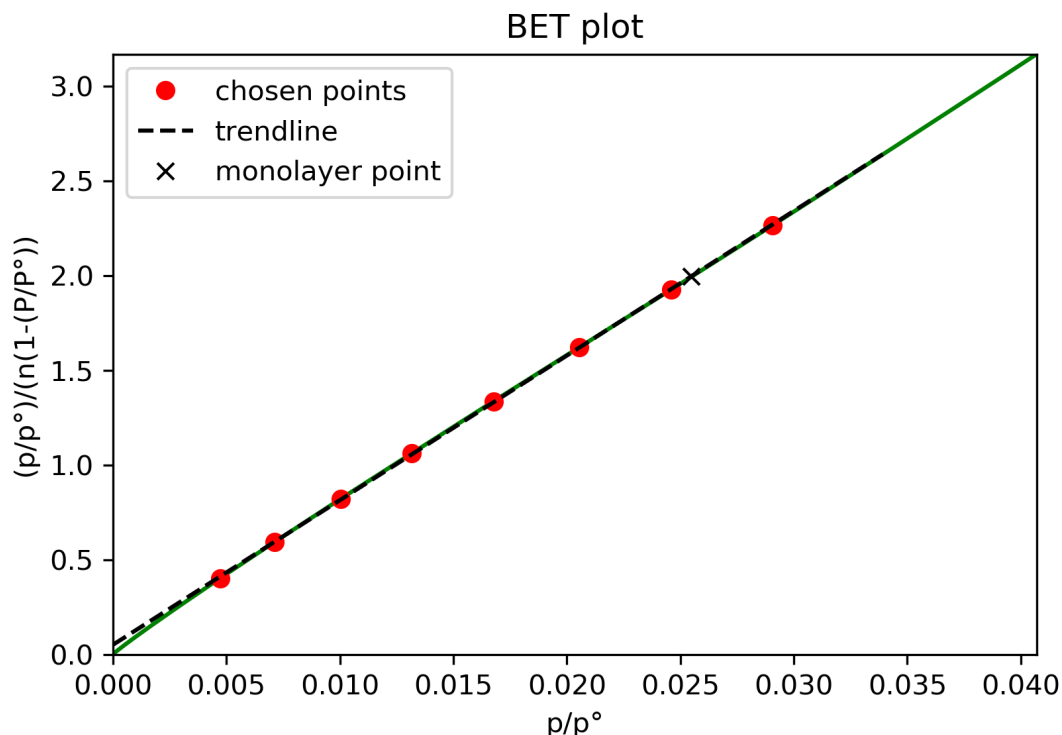


Figure 1.1: BET transformation and point selection

```
pygaps.dft_size_distribution(iso, kernel_path='internal')
```

The DFT fitting is done using the internal kernel which is applicable for N<sub>2</sub> on carbon slit pores and included with pyGAPS. Results are shown in Figure 1.2. We can see that whilst both methods produce a bimodal size distribution, neither is accurate in describing the crystallographic pore widths. This is to be expected, since neither method is applicable to the UiO-66(Zr) system. However, when comparing two samples of the same MOF, these methods can still highlight differences in the quality of the two batches. For example, it can be seen that the DFT method shows wide peaks at >1 nm which can be an indication of the presence of defects in the UiO-66(Zr) structure. Indeed, TGA analysis of the pristine sample shows a linker ratio (11.8 linkers per cluster) that is lower than it would be in a perfect sample (see figure in supplemental information.)

New materials are often screened for their ability to act as a CO<sub>2</sub> capture material. A good predictor of performance in this application are the enthalpies of adsorption, which are an indication of host-guest interactions. Here, we first measure the differential heats of adsorption directly through the use of adsorption microcalorimetry at 303 K. Then, to determine the isosteric heats of adsorption, two isotherms have been measured at 303 K and 323 K respectively. The complete set of isotherms is loaded into pyGAPS and plotted by the `pygaps.plot_iso()` function as seen in Figure 1.3a. To calculate the isosteric heat of adsorption, the two isotherms measured for this purpose are passed through the `pygaps.isosteric_heat()` function. The results from the calculation are overlaid on

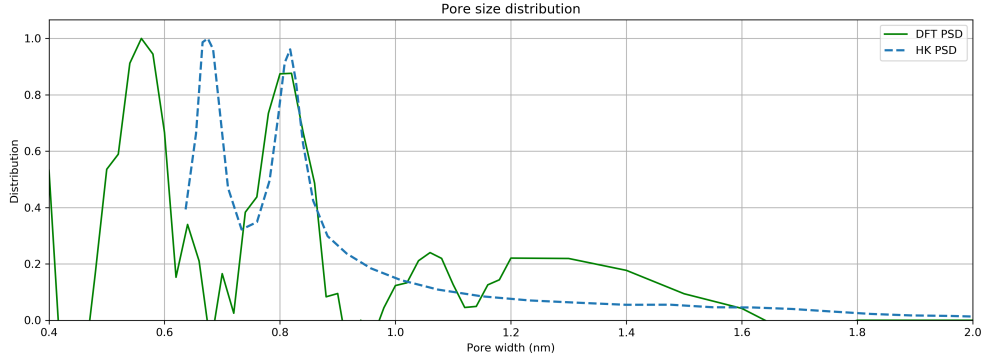


Figure 1.2: Pore size distribution calculated through the Horvath-Kawazoe method (dotted blue line) and the internal DFT kernel (continuous green line)

top of the measured calorimetric data in Figure 1.3b. The two datasets are overlap for the most part but diverge at low loadings and near complete coverage. At low loading the small changes in pressure amount introduce large errors in the Clausius-Clapeyron equation. This, together with the breakdown of the assumption of equilibrium due to active sites in the MOF lead to the calorimetric measurement providing more valid results. At higher loadings, where the isotherm reaches a plateau and the change in adsorbed amount is small from point to point, errors are introduced in the direct calculation of the heat of adsorption. The two techniques are thus complementary.

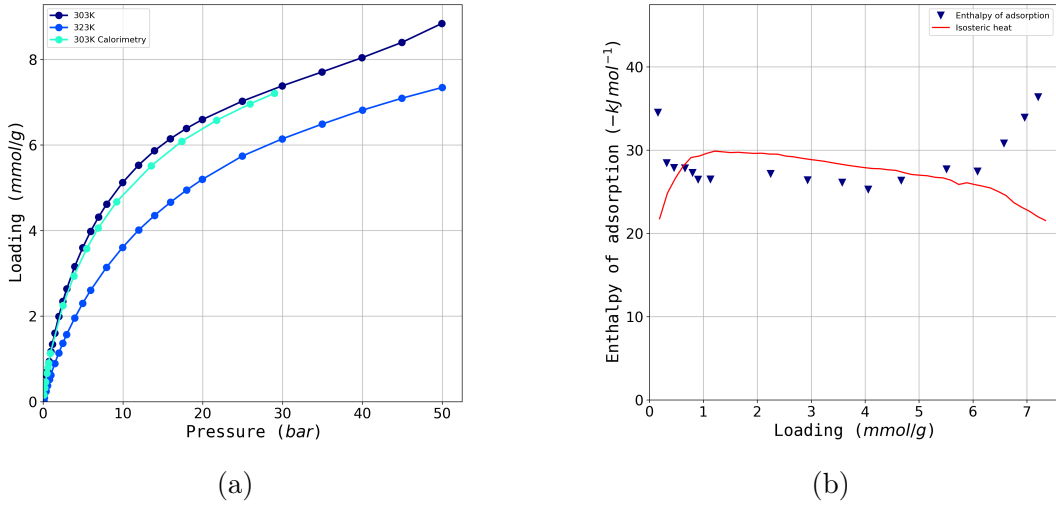


Figure 1.3: Calculation of enthalpy of adsorption: (a) the dataset of isotherms used and (b) the calculated isosteric heat (red line) together with the measured differential enthalpy of adsorption (blue triangles)

### 1.4.2 Analysis of a carbon sample for gas separation applications

A sample of reference carbon Takeda 5A is to be investigated for an in-depth characterisation of the adsorption behaviour of pure gases, with a focus on describing the pore environment. Afterwards, the performance of different binary separations is evaluated, such as CO<sub>2</sub>/N<sub>2</sub> and propane/propylene.

Pure gas adsorption data has been recorded at 303 K in conjunction with microcalorimetry on N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>. The complete dataset is plotted with the `pygaps.plot_iso()` function and can be seen in Figure 1.4a.

Nitrogen and carbon monoxide are similar in their adsorption behaviour, with a nearly linear isotherm and low capacities. Hydrocarbons are adsorbed with higher loadings, with both propane and propylene reaching a plateau at low pressures. Propylene is seen to have a higher capacity than propane, with packing effects as a likely cause. Carbon dioxide has the highest loading capacity of the entire dataset.

Two parameters can be useful in characterising the local pore environment before guest-guest interactions come into effect: the Henry constant at low loadings as well as the initial enthalpy of adsorption. Both can be calculated with `pyGAPS`, with several options in regard to the methodology. Here, Henry’s constant is calculated using the `pygaps.initial_henry_virial()` function, which fits a virial model to the isotherm and then takes the limit at loading approaching zero. The initial enthalpy of adsorption is obtained through the `pygaps.initial_enthalpy_comp()` function. This fits the enthalpy curve to a compound contribution from guest-host interaction, defects, guest-guest attraction and repulsion using a minimization algorithm. The results of the calculations are plotted versus the polarizability of the gas used, which can be obtained from the respective `Adsorbate` class. Figure 1.4b shows that both the parameters fall on a linear trend, which suggests that the interactions between those guests and the pore walls are mostly due to Lennard-Jones interactions. Carbon dioxide has a higher enthalpy of adsorption than the baseline due to the contribution from its quadrupole moment. There is almost a complete overlap between propane and propylene, which leads to the conclusion that the unsaturated double bond does not interact in a specific way with the carbon surface. The difference between the two isotherms is due exclusively to steric and packing effects.

From the analysis of the pure gas dataset and the property-polarizability graph, two potentially interesting separations arise, namely CO<sub>2</sub>-N<sub>2</sub> and propylene-propane. For these two pairs we use ideal adsorbed solution theory (IAST) to simulate binary adsorption behaviour. The `pyGAPS` framework includes a modified version of the `pyIAST` code<sup>(?)</sup> which has been adapted to work with the `Isotherm` classes. Both model isotherms and real data can be used for IAST, with spreading pressure being calculated through the underlying isotherm model or through interpolation, respectively. Based on the previous analysis, we expect to see good performance for carbon dioxide capture and little or no selectivity in the paraffin-olefin pair.

In this case, we fit the experimental data to the available models in `pyGAPS`, then use the resulting model isotherms for IAST simulations. In order to get a ‘best-fit’ model isotherm, we use the function in Listing 1.2, which fits all available models and

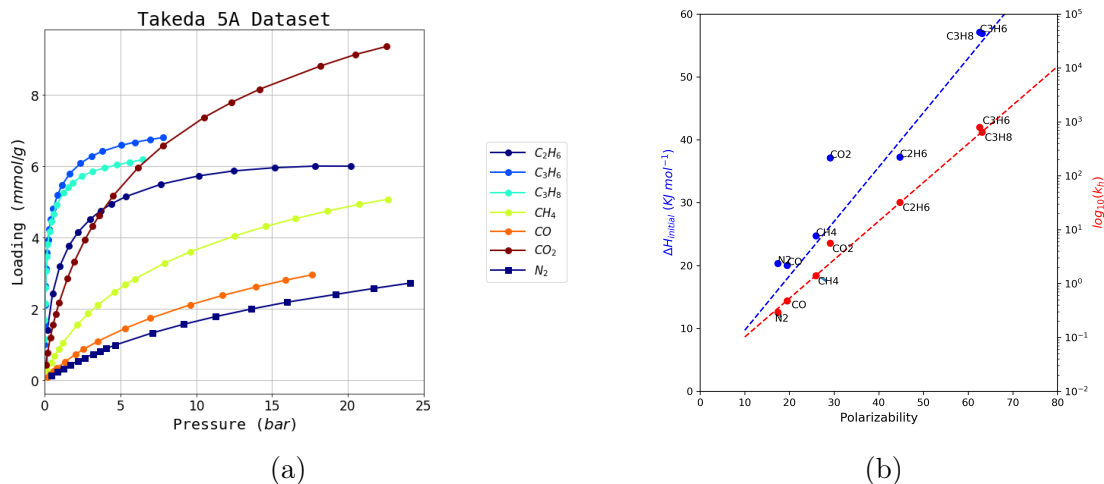


Figure 1.4: Takeda 5A dataset processing: (a) the experimental dataset all recorded gases and (b) the calculated trends of initial heat of adsorption and Henry's constant

selects the one with the lowest residuals between the fitted function and the real data. Currently, the models available in `pyGAPS` are: Henry, single, double and triple site Langmuir, (?) BET, (?) Quadratic, (?) Jensen-Seaton, (?) Toth, (?) Tempkin approximation, (?) Virial, (?) and the Flory-Huggins (?) and Wilson (?) variations of Vacancy Solution Theory (VST). The isotherms and their best-fitting model is displayed in Figure 1.5a for the  $CO_2$ - $N_2$  pair and in Figure 1.6a for the  $C_3H_8$ - $C_3H_6$  pair.

Listing 1.2: Guessing the best model

```
model = pygaps.ModelIsotherm.from_pointisotherm(iso, guess_model=True)
```

For the carbon dioxide separation, we simulate all equilibrium points for the adsorbed and gaseous phases at different concentrations of the two gases at 1 bar. To do this we use the `pygaps.iast_vle()` function which produces an analogue of a vapour-liquid equilibrium at a specified pressure for a binary mixture. The resulting graph of this function can be seen in Figure 1.6b. As expected, the predicted adsorbed mixture is rich in carbon dioxide. Selectivity can also be calculated in a single point, with the value at 15%  $CO_2$  and 1 bar being 16.5.

For the propane-propylene separation, we simulate the selectivity for propane within a pressure range for a 50% mixture of the two gases. It can be seen that there is little or no preference for the unsaturated molecule, though the selectivity increases slightly at pressures above 1 bar.

## 1.5 Conclusion

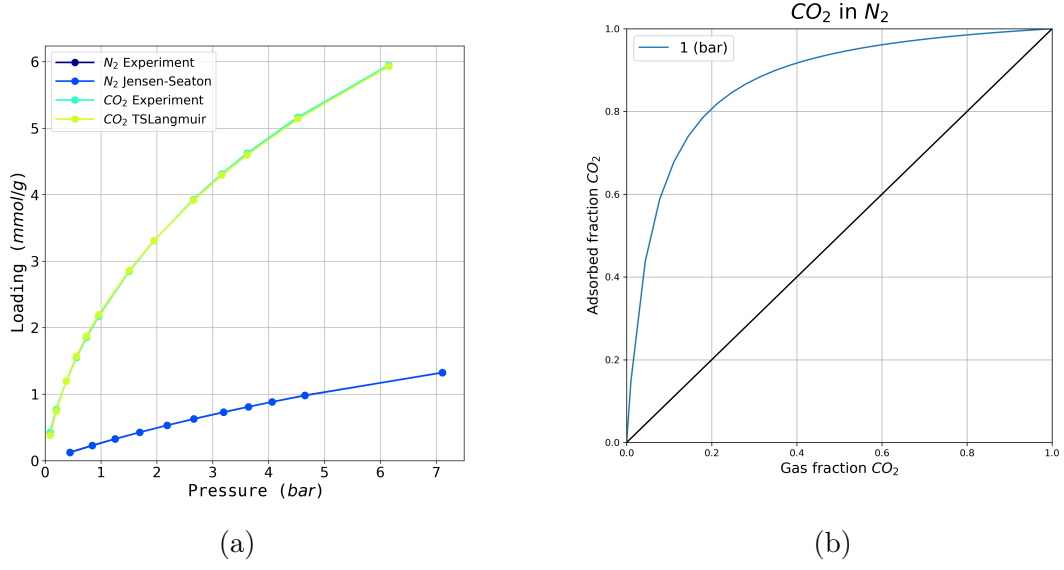


Figure 1.5: Modelling binary adsorption of  $CO_2$  and  $N_2$ : (a) the pure component isotherms and their best fit models and (b) the predicted composition of the gaseous and adsorbed phase for different fractions of  $CO_2$  at 1 bar

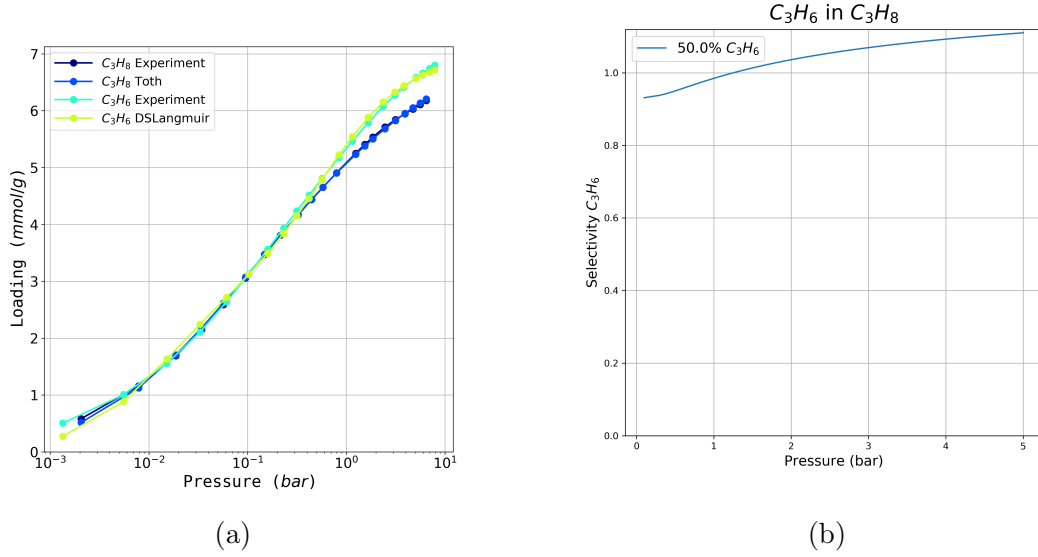


Figure 1.6: Modelling binary adsorption of a propane-propylene mixture: (a) the pure-component isotherms and their best fit models and (b) the predicted selectivity of propane adsorption of a 50-50% mixture in a range of pressure from 0.1 to 7 bar

# Common characterisation techniques

## 1 Thermogravimetry

TGA experiments were carried out on ca. 15 mg sample with a Q500 (TA Instruments) apparatus in a dynamic “Hi-Res” mode using  $3\text{ K min}^{-1}$  under both nitrogen and argon flow at  $30\text{ cm}^3\text{ min}^{-1}$ . For comparison, the curves have been normalized at  $800\text{ }^\circ\text{C}$ .

## 2 Bulk density determination

Bulk density was determined by weighing 1.5 ml empty vessels and settling the powder or the spheres of the MOFs inside. Powders have been added by small increments and settled through vibration between each addition. We finally weighed the full vessels, which allowed the bulk density to be determined. The experiments were recorded with the same vessel after cleaning.

## 3 Nitrogen physisorption at 77 K

Nitrogen physisorption at 77 K was used to calculate BET areas and accessible pore volumes.<sup>(?)</sup> Approximately 60 mg of sample were used for each measurement. The adsorption experiments were carried out on a Micromeritics Triflex apparatus. The BET area on these microporous solids was calculated using the procedure devised by ? Accessible pore volume was calculated from the amount adsorbed at  $p/p^0 = 0.2$ . The pore sizes were calculated by applying the Dollimore-Heal method on the desorption branch of the isotherm.

## 4 Gravimetric isotherms measured on Rubotherm Balance

The gravimetric isotherms in this study were obtained using a commercial balance (Rubotherm GmbH). Approximately 1 g of dried sample was used for these experiments. Samples was activated in situ by heating under vacuum. The gas was introduced using a step-by-step method, and equilibrium was assumed to have been reached when the variation of weight remained below  $30\text{ }\mu\text{g}$  over a 15 min interval. The volume of the sample was determined from a blank experiment with helium as the nonadsorbing gas and used in combination with the gas density measured by the Rubotherm balance to compensate for buoyancy.

## **5 Vapour adsorption**

Adsorption of water or ethanol vapour was measured at 298 K on a BELmax apparatus (MicrotracBEL, Japan). Approximately 50 mg of material was used for each experiment.