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A STUDY OF HETEROGENEITY OF BARIUM SULPHATE SURFACES
PARTIALLY COVERED BY ADSORBED MATERIAL

by

SURESH SUNDERLAL PATEL, M.Sc.

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy at Loughborough University of Technology

November 1987

Supervisors:   M.J. Jaycock, Ph.D
               Department of Chemistry
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               Unilever Research

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DEDICATION

To my parents and wife
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DECLARATION OF ORIGINALITY

The work in this thesis is the original work of the author throughout the text, except where otherwise acknowledged, and has not been presented previously, wholly or in part, for the award of any degree in any University.
The main objective of this work was to study the sensitivity of the Heterogeneity Analysis surface characterisation methods in the detection of the surface modification of barium sulphate due to the presence of various amounts of preadsorbed sodium tripolyphosphate (STPP). The main method considered was HILDA (1974) and three isotherms were also analysed using CAEDMON (1975).

A series of adsorbates: krypton, argon, nitrogen and carbon monoxide were used to probe the surface of barium sulphate. Precipitated barium sulphate was prepared and solution adsorption isotherms of STPP were determined at pH 7.6 and pH 9.0. The barium sulphate samples were characterised by the following techniques: x-ray diffraction, electron spectroscopy for chemical analysis and scanning electron microscopy.

A grease and mercury-free volumetric adsorption apparatus was employed which consisted of four pressure gauges ranging from $10^{-5}$ to $10^{3}$ mmHg. All the adsorption measurements were determined with great accuracy and detail at 77.8K. Isosteric heats were estimated from nitrogen adsorption isotherms at 77.8, 80.8 and 81.6K on barium sulphate.

The Heterogeneity Analysis was used to analyse the nitrogen and carbon monoxide data for the preadsorbed samples, which showed the high energy sites present on the surface of barium sulphate were reduced considerably by adsorbing STPP. Furthermore, within the HILDA method, the Langmuir, Hill-de Boer and Fowler-Guggenheim models were compared, methods of termination of the data was investigated, and the stability of results was studied. A normalisation procedure for submonolayer data was applied.

The specific surface area of the samples used were estimated and compared with various adsorbates, different batches of barium sulphate and increasing coverage of STPP.
INTRODUCTION

The measurement of the physical adsorption of gases, in particular nitrogen and inert gases, has been extensively used to investigate surface properties of solids. The specific surface area, the distribution of pore sizes and enthalpies and entropies of adsorption have all been measured. Recently much interest has been shown in the study of heterogeneity of solid surfaces.

1.1 The Origins of Surface Heterogeneity

All solid surfaces possess some form of intrinsic heterogeneity caused by the periodic nature of the adsorptive potential energy field. If the intrinsic heterogeneity is small (i.e. the free energy barrier to adsorbate translation is small), the surface tends towards a unisorptive substrate. In a real system heterogeneity may arise from the following sources:

(i) Edges of crystals
(ii) Corners (i.e. where two or more edges meet)
(iii) Kinks (i.e. inverted corner with a plane missing, which causes a triangular hole)
(iv) Spiral growth
(v) Schottky and Frenkel defects
(vi) Dislocations
(vii) Multiplicity of crystal planes
(viii) Surface impurities or variation of surface groups.

Because of the widespread occurrence and use of heterogeneous surface adsorbents it is important that the adsorption phenomena associated with them be well characterised and understood, and that techniques for uniform surfaces be extended to provide the maximum amount of information on such surfaces.
1.2. **Theoretical Approach to the Analysis of Experimental Adsorption Isotherms**

There has been a long history of theoretical interest in the quantitative description of surface heterogeneity since the pioneering work of Langmuir (1918), and in the past 30 years there have been various attempts to determine the heterogeneity of a solid surface. Halsey (1951) used the multilayer adsorption theory, however difficulties arose in distinguishing monolayer sites of low energy from multilayer sites, and the exact form of the decrease in adsorption energy with multilayer formation.

Drain and Morrison (1952) extrapolated the measured heats of adsorption at 85K to estimate the isosteric heat of adsorption of argon on TiO$_2$ at 0K, $\Delta H^*_{iso}$, and obtained a distribution function of energy sites directly from the slope of the plot of $\Delta H^*_{iso}$ against the volume of gas adsorbed. Difficulties arose at higher surface coverage however, when the value of $\Delta H^*_{iso}$ is determined mainly by interactions between the adsorbed atoms, and not by the properties of the surface.

Ross and Olivier (1964) described heterogeneity by a number of "patches" of different adsorption energy. Using this patchwise model the integral equation for the adsorption isotherm on a heterogeneous surface is of the general form:

$$\Theta_E = \int_0^\infty F'(U)\Theta_m(P,U)dU$$  \hspace{1cm} (1.1)

where $\Theta_E$ is the fractional monolayer coverage of the surface, $F(U)$ is a numerical function of the fraction of the surface with energies $U$ or less, hence $dF(U)/dU = F'(U)$, is the frequency of
"patches" per unit energy interval and $\Theta_m(P,U)$ is the model isotherm function for a single patch; $U$ is equal to the maximum adsorption energy, $U_m$, minus the zero state vibrational energy, and is taken as positive in magnitude. This integral is an equation for $F'(U)$ with the kernel given by the model isotherm function. Hence, this equation allows us to characterise the adsorbent by $F'(U)$, the distribution function or site energy distribution function (SED). Adamson and Ling (1961) have noted that this energy distribution function may be the dominating factor in adsorption on heterogeneous surfaces, as well as their most uniquely characterisable feature.

This integral equation relates the energy distribution function to the experimental adsorption isotherm and has been solved analytically for $F'(U)$ for homotattic surfaces in certain cases. This term was introduced by Sanford and Ross (1954) who defined a homotattic surface as the surface of a submicroscopic patch or region which forms part of a larger surface, but acts as if its structure were uniform and homogeneous. A number of numerical methods have been applied to eqn. 1.1 to calculate $F'(U)$.

1.2.1. The Work of Adamson and Ling

The method of Adamson and Ling (1961) determines the function $F'(U)$ from the experimental adsorption isotherm and an assumed local isotherm function. The method is graphical so that it is not necessary to represent either the experimental adsorption isotherm or the local adsorption isotherm function analytically, and successive approximations are used. The site energy distributions are temperature-independent,
and are consistent with isosteric and differential heats of adsorption (Drain and Morrison, 1952). This iterative method has been used by Dormant and Adamson (1972), House and Jaycock (1974) and Waksmundzki et al (1975).

1.2.2. The Ross and Olivier Graphical Method

Ross and Olivier (1964) calculated total adsorption isotherms assuming a Gaussian distribution function of width $\gamma$, and the Hill-de Boer equation for the uniform adsorption model. They fitted calculated isotherms to experimental adsorption isotherms, to determine the heterogeneity parameter $\gamma$. This method was also used by Jaycock and Waldsax (1971) and House and Jaycock (1974).

1.2.3. CAEDMON

Ross and Morrison (1975) have described a computer-based method known by the acronym CAEDMON (Computed Adsorptive Energy Distribution in the MONolayer) for obtaining $F'(U)$. The heterogeneous surface is modelled as a collection of up to twenty homotattic patches of different adsorptive energy. The isotherm describing adsorption on a given patch is given by an approximation to the virial equation of state, and the overall adsorption is calculated by a summation over all the patches. An initial distribution is arbitrarily chosen, then systematically adjusted using a multivariate Newton-Raphson technique to minimise the deviation between the experimental adsorption isotherm and that calculated from the distribution. Using the program to analyze isotherm data for nitrogen and argon on a series of carbon blacks, the $F'(U)$ calculated showed the increasing uniformity of the surface with increased graphitization.
1.2.4. HILDA

House and Jaycock (1978) presented the HILDA (Heterogeneity Investigated at Loughborough by A Distribution Analysis) algorithm, which is an iterative numerical method based upon the graphical technique of Adamson and Ling. An initial distribution is obtained assuming step functions for the local isotherms, then this approximation is improved upon iteratively until the root mean square (rms) deviation between the experimental and calculated isotherm is sufficiently small. Unlike the CAEDKON algorithm, the HILDA algorithm updates the entire distribution at once. A discussion on the advantages and shortcomings of the two techniques was reported by Morrison and Ross (1977) and Dormant and Adamson (1977).

The HILDA program has been used in the analysis of the energy distributions for inert gases adsorbed on sodium chloride (House, 1975) and Krypton adsorbed on silver iodide (Sidebottom et al, 1976). HILDA has been compared to the CAEDMON algorithm using the data for the adsorption of Krypton on silver iodide and nitrogen on Spheron 6 (House and Jaycock, 1977). It was noted that, although HILDA program required more computer core space (18k vs. 9k), it executed over eighty times faster than did CAEDMON when the data of silver iodide was used. The main result of the comparison was that both programs gave very similar energy distributions for this sample. From the energy distributions, the energies at which the peak occurred closely coincided, with those from HILDA more sharply defined. For the nitrogen data, HILDA predicted a number of sharp peaks, and the CAEDMON energy distribution was broader with fewer peaks. The results were in general good agreement with each other, with the CAEDMON result appearing to be a less resolved form of the HILDA energy distribution.
Agreement between energy distributions calculated by HILDA and by a regularisation method (House, 1978a) has been observed for the case of adsorption of hydroxylated non-porous silica (House, 1978a).

1.2.5. Other Algorithms for Energy Distributions

House et al. (1981) investigated the surface heterogeneity effects in nitrogen adsorption on chemically modified aerosils. Four numerical methods i.e., HILDA, Jaroniec's method, Brauer's method and CAEDMON 2 were used to study the various chemically modified aerosils. The HILDA and CAEDMON algorithms indicated similar energy distributions for nitrogen adsorption on the aerosils.

1.3. Results of Analysis

Leng and Clark (1982) have used HILDA to investigate surface modifications due to heat treatment of silica using nitrogen and krypton as the gas probes in the pressure range $10^{-5}$-1 mmHg. The energy distributions obtained using krypton on silica were found to be roughly of the form of an exponential decay with increasing adsorption energy and with few structural features. This was in agreement with the results of House (1978a) for the energy distributions of argon on silica from both the HILDA and the regularization methods.

House et al. (1984) have recently studied the surface heterogeneity of highly dispersed silicas modified chemically by treatment with sodium and potassium hydroxide using nitrogen as the gas probe. The HILDA algorithm and the condensation approximation with Jaroniec's method were used to determine the energy distributions. Both these methods produce the same general shape for the energy distributions,
although the HILDA energy distribution showed greater structural detail. From this work the energy distributions showed that increasing the alkali content of the silica increased the density of the high energy adsorption sites. Also, the specific surface area determined by conventional BET method (Brunauer et al., 1938), decreased with increasing the alkali content of the silica.

The work on surface heterogeneity that has been reviewed above has given valuable information on various adsorbents i.e. sodium chloride, silver iodide, graphitized carbons and silicas, which have been compared with physical and chemical treatment. It is the objective of this work to study the sensitivity of the HILDA method to precipitated barium sulphate with various amounts of preadsorbed sodium tripolyphosphate (STPP). No previous work has been reported on such a system.

1.4. Barium Sulphate and the Scaling Problem

This system was investigated as scaling is a major problem in the chemical industry. It is a result of the precipitation of slightly soluble salts from solution onto the walls of the vessel, and it is hard to redissolve and strongly adherent. Scale is formed when supersaturation of one or more of the salt is exceeded.

This problem is chiefly encountered in water treatment and desalination plants, where the precipitation and growth of calcium salts (i.e. sulphate hydrates, carbonate polymorphs and phosphates) from natural water occurs. These scale deposits lower the heat transfer coefficient at the heated metal surfaces and reduce the thermal efficiency of the desalination process, which significantly
increases the cost of producing potable water. In some instances, such as calcium carbonate and phosphate scales, the problem can be reduced by lowering the pH of the medium. However, this may lead to undesirable acid attack on metal surfaces, and for large volumes of solution, this method is not economically feasible.

In the petroleum industry, scaling arises from a specific set of geological, physical and chemical conditions. Geological factors such as ground water circulation and mineral composition may mediate in scale formation as may physical factors such as pumping rates and well pressure. However, the significant factor in regulating scale formation is chemical.

The minerals that appear to cause the most serious problems in oil-well scaling are the sulphates of calcium and barium, and calcium carbonate. Calcium sulphate and calcium carbonate have solubilities that decrease with increasing temperature, thus a higher ambient temperature in the down hole encourages the formation of the scale deposits of these minerals. Barium sulphate presents a particularly serious problem because it is very insoluble and cannot be dispersed once it has deposited as scale.

In order to alleviate the scale problem, it has been shown by many workers (Sung-Tsuen and Nancollas, 1975; Rizkalla, 1983; Miura et al, 1962; Leung and Nancollas, 1978; van Rosmalen et al, 1982; and Smith, 1982) that trace amount of crystal growth inhibitors vastly reduce scale formation. These crystal growth inhibitors are inorganic polyphosphates eg Triphosphate, Tetraphosphate, Pentaphosphate and Hexaphosphate (Miura et al, 1962, 1963; Sung-Tsuen, 1975; Leung and Nancollas, 1978; Rizkalla, 1983) are effective
inhibitors of calcium carbonate and barium sulphate. However, at high temperatures, the polyphosphates hydrolyse to orthophosphate which may contribute to scale formation. The organic phosphonates eg ethylenediaminetetra(methylene phosphonic)-acid, hexamethylene-diaminetetra (methylene phosphonic)acid, diethylene-triaminepenta-(methylene phosphonic) and 1,hydroxyethane-1,1-diphosphonic acid (Sung-Tsuen, 1975; van Rosmalen et al., 1982, 1980; Leung and Nancollas, 1978) are potent inhibitors which have recently been developed, and may be used in a variety of practical situations due to their thermal stability. The polyelectrolytes eg poly(acrylic acid) (Leung and Nancollas, 1978), isobutylene/maleic anhydride copolymer (Williams and Ruehrwein, 1957) and poly(methacrylic acid) (Crawford and Smith, 1966) have also been used to inhibit the growth of calcium sulphate and carbonate.

Other alternative crystal growth inhibitors, besides the three major classes given above are inorganic anions and cations (Botsaris, 1982; Smith, 1982), surfactants and mucopolysaccharides (Smith, 1982). These have specific interactions with certain mineral scales and cannot be used generally.

Our understanding of the mechanism by which these crystal growth inhibitors affect crystal growth is limited on the basis of earlier work, several models have been proposed for the crystal growth mechanism (Nancollas, 1979). It is widely assumed, though with notable exception (Glasner, 1969; Sarig et al., 1973), that inhibitors act by adsorbing on specific high energy sites on a crystal surface (Nancollas et al., 1976; Reddy and Nancollas, 1973), i.e. those sites at which growth is most favourable (e.g. steps, kinks, edges, dislocations, etc) thus preventing the attachment of lattice ions.
1.5. The Scope of the Present Study

The aim of this study is to utilise the surface heterogeneity method to characterise barium sulphate with various amounts of STPP. It is also intended to compare various local isotherm functions within the scope of the heterogeneity analysis and use the multilayer BET method (Brunaur et al., 1938) for the estimation of specific surface areas of the samples investigated.

Chapter 2 describes the theoretical aspects of the determination of energy distributions. The preparation and physical characterisation of barium sulphate with various amounts of STPP is presented and discussed in Chapter 3. Followed by the determination of the gas adsorption isotherms for these samples with nitrogen, krypton, argon and carbon monoxide at liquid nitrogen temperatures using a volumetric method (Chapter 3). Chapter 4 presents the experimental adsorption isotherms, the energy distributions obtained from the heterogeneity analysis and the estimation of the specific surface area results.

Chapter 4 presents and discusses the individual results which are sectioned into the following themes:

1. Barium sulphate with various amounts of STPP.
2. Normalization procedure for submonolayer data.
3. Carbon monoxide as a gas probe.
4. CAEDMON method.
5. Adsorption of different adsorbates onto barium sulphate.
6. Comparison of two samples of barium sulphate.
7. The effect of adsorption temperature.

The broader and diverse aspects of the discussions are presented in Chapter 5 in the form of conclusions.
CHAPTER 2

THEORY
2.1. **Surface Heterogeneity**

The origins of surface heterogeneity have been presented in Section 1.1. An attempt can be made to determine the surface heterogeneity of a solid by using models for adsorption onto uniform surfaces and experimentally determined adsorption isotherms from which a distribution of adsorptive potentials may be obtained. This distribution of adsorptive potential or SED describes the surface of the solid and the interaction of the gas to that solid surface.

2.1.1. **Random and Patchwise Models**

When analysing experimental isotherms, the degree of heterogeneity of the surface is very important if meaningful results are to be obtained. Most of the classical equations that have been widely used e.g. Langmuir and Hill-de Boer equations, are strictly applicable to homogeneous surfaces. To overcome this problem two models have been suggested: the random model (Hill, 1949) has been investigated by Steel (1963), but is impractical and physically unrealistic as for most surfaces a completely random distribution of sites is not expected, and the "patchwise" model proposed by Ross and Olivier (1964), which has been more successful. In the latter approach, the heterogeneity is described by a number of patches of different adsorption energy. The major assumption implicit in this model is that adsorbate-adsorbate interactions may be included within a patch, but that no lateral interactions between atoms in patches of different energies are considered. Using this patchwise
model the integral equation 1.1 may be written for a heterogeneous surface:

\[
V_a(P) = V_m \int_0^\infty F'(U) \theta_m(P,U) \, dU
\]  
(2.1)

where \(V_a(P)\) is the amount of gas adsorbed at the equilibrium pressure \(P\), and \(V_m\) may be the monolayer coverage or simply a normalising factor such that:

\[
\int_{U_{\text{min}}}^{U_{\text{max}}} F'(U) \, dU = 1
\]  
(2.2)

depending on the range of energies \((U_{\text{min}}, U_{\text{max}})\) covered by the experimental isotherm data.

2.2. Model Isotherm Functions

2.2.1. Hill-de Boer Equation

The Hill-de Boer isotherm equation (de Boer, 1968) is the two-dimensional analogue of the van der Waals equation. It represents a mobile adsorbed film and includes the effect of lateral interactions of adsorbate molecules. The Hill-de Boer equation is:

\[
P = K \frac{\theta}{1 - \theta} \exp \left[ \frac{\theta}{1 - \theta} - \frac{2a\theta}{\beta kT} \right]
\]  
(2.3)

Equation 2.3 is in the generalised form for the model isotherm function:

\[
P = K g(\theta, T)
\]  
(2.4)

where \(K\) is given by:

\[
K = A^* (-U/kT)
\]  
(2.5)

in which \(A^*\) is a constant for a particular isotherm function, \(K\) is
an integration constant dependent only on interactions between adsorbate and adsorbent, \( P \) is the pressure, \( \theta \) is the coverage, \( k \) is the Boltzmann constant, \( T \) is the temperature and \( \alpha \) and \( \delta \) are the analogues of 'a' and 'b' in the van der Waals' equation. If any lateral interactions are being described in the isotherm function, they are contained in \( g(\theta, T) \).

If the adsorbate is below its critical temperature a phase transition from gas to two-dimensional fluid will occur at \((P/K)_{\text{step}}\).

If the adsorption temperature is above the experimental critical temperature, the approximating step function \( \theta_m(P_i, U_i) = 1 \) for \( U > U_i \) and \( \theta_m(P_i, U_i) = 0 \) for \( U < U_i \) is taken through the point of inflection \((P/K)_{\text{step}}\) at \( \theta_i \). In both cases \( U_i \) may be determined from:

\[
U_i = kT \left[ \ln A^* - \ln \left( \frac{P_i}{(P/K)_{\text{step}}} \right) \right] \quad (2.6)
\]

From equation 2.6 it can be seen that the effect of \( \ln A^* \) is to translate the adsorptive energy scale of the distribution.

If \( K \) is known, \( \ln A^* \) may be used to obtain \( U \). A low temperature approximation may be used to calculate \( \ln A^* \) i.e.

\[
\ln A^* = \ln \left[ \frac{\left( \frac{2\pi m kT}{h^2} \right)^{1/2} kT}{\delta^3} \right] \quad (2.7)
\]

where \( m \) is the atomic mass.

In this evaluation, the units of \( A^* \) must be those of pressure.
The values of $\alpha$ and $\beta$ in the Hill-de Boer equation corresponds to 'a' and 'b' values in the van der Waals equation:

$$\alpha = a \left[ \frac{9\pi}{256b} \right]^{1/3} \text{ and } \beta = 2b \left[ \frac{9\pi}{256b} \right]^{1/3}$$

so that:

$$\frac{\alpha}{\beta} = \frac{a}{2b}$$

2.2.2. The Langmuir Equation

The derivation of the Langmuir equation is well known (Hill, 1960). Written in the form of equation 2.4:

$$g(\theta, T) = \frac{\theta}{1 - \theta}$$

It represents a localised adsorbed film on a uniform surface and does not take account for lateral interactions of adsorbate molecules. To calculate $\ln A^o$ for the Langmuir model, House (1975) used the following low temperature approximation:

$$\ln A^o = \ln \left[ \frac{2\pi m kT}{u^2} \right]^{3/2}$$

Tables 2.1 and 2.2 show the Langmuir model constants used in this study.
TABLE 2.1 Parameters that were used in the HILDA analysis

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>TEMPERATURE /K</th>
<th>MODEL</th>
<th>MODEL ISOTHERM CONSTANTS</th>
<th>ln A°</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>θ₁</td>
<td>θₜ</td>
<td>(P/K)_{step}</td>
</tr>
<tr>
<td>N₂</td>
<td>77.8</td>
<td>HdB</td>
<td>0.3163196</td>
<td>0.3163196</td>
<td>0.1290154</td>
</tr>
<tr>
<td>N₂</td>
<td>77.8</td>
<td>LANGMUIR</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>N₂</td>
<td>80.8</td>
<td>HdB</td>
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<td>0.3104325</td>
<td>0.1362579</td>
</tr>
<tr>
<td>N₂</td>
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<td>LANGMUIR</td>
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<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>N₂</td>
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<td>HdB</td>
<td>0.3071501</td>
<td>0.3071501</td>
<td>0.1398278</td>
</tr>
<tr>
<td>N₂</td>
<td>81.6</td>
<td>LANGMUIR</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>
### Table 2.2 Parameters that were used in the HILDA analysis

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>TEMPERATURE /K</th>
<th>MODEL</th>
<th>MODEL ISOTHERM CONSTANTS</th>
<th>ln A°</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>θₐ</strong></td>
<td><strong>θₐ</strong></td>
<td>(P/K)step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>77.8</td>
<td>HdB</td>
<td>0.059069669 0.680784600</td>
<td>0.039281541</td>
<td>14.686</td>
</tr>
<tr>
<td>Kr</td>
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<td>FG</td>
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<td>0.1159032</td>
<td>13.6998</td>
</tr>
<tr>
<td>Kr</td>
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<td>LANGMUIR</td>
<td>0.5 0.5</td>
<td>1.0</td>
<td>20.511</td>
</tr>
<tr>
<td>Ar</td>
<td>77.8</td>
<td>HdB</td>
<td>0.3326481 0.3326481</td>
<td>0.09442162</td>
<td>14.453</td>
</tr>
<tr>
<td>Ar</td>
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<td>LANGMUIR</td>
<td>0.5 0.5</td>
<td>1.0</td>
<td>19.391</td>
</tr>
<tr>
<td>CO</td>
<td>77.8</td>
<td>HdB</td>
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<td>14.139</td>
</tr>
<tr>
<td>CO</td>
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<td>LANGMUIR</td>
<td>0.5 0.5</td>
<td>1.0</td>
<td>18.858</td>
</tr>
</tbody>
</table>
2.2.3. The Fowler-Guggenheim Equation

As with the Langmuir equation, the Fowler-Guggenheim equation (Fowler and Guggenheim, 1956) is based on a localised model of adsorption, but includes average nearest neighbour interactions. The isotherm equation is:

\[ P = k \left[ \frac{\theta}{1-\theta} \exp\left(-\frac{ZW\theta}{kT}\right) \right] \]  \hspace{1cm} (2.12)

where \( W \) is the nearest neighbour interaction energy and \( Z\theta \) is the number of occupied nearest neighbour sites. The Fowler-Guggenheim equation shows a two dimensional gas-liquid phase transition when \( ZW/kT > -4 \). The values of \( \theta_l \) and \( \theta_h \) below the critical temperature may be obtained from the symmetry condition:

\[ \theta_l - 1 = \theta_h \]  \hspace{1cm} (2.13)

with the corresponding \((P/K)_{\text{step}}\) value obtained from substituting \( \theta = 0.5 \) in equation 2.12. The \( \theta_l \) and \( \theta_h \) values may then be obtained by a "half-step" iterative procedure using equation 2.12 above the critical point \( \theta_l = 0.5 \).

The value of \( ZW \) is usually taken as a fraction of the corresponding heat of vapourisation or liquifaction of the bulk gas. Table 2.2 shows the Fowler-Guggenheim model constants used in this study.
2.3. **Iterative Method of HILDA**

2.3.1. **Solution for F'(U)**

For $N$ experimental isotherm data points, a set of equations may be written:

$$
V_a(P_1) = V_m \int_{m_0}^{\infty} F'(U) \theta_m(P_1, U) dU \\
V_a(P_2) = V_m \int_{m_0}^{\infty} F'(U) \theta_m(P_2, U) dU \\
\vdots \\
V_a(P_N) = V_m \int_{m_0}^{\infty} F'(U) \theta_m(P_N, U) dU
$$

(2.14)

The solution for $F'(U)$ or $F(U)$ is required such that the root mean square (r.m.s.) deviation between the calculated values of $V_a$ and the experimental determination, $V_a^{\exp}$, is a minimum:

$$
\text{r.m.s.} = \left( \frac{1}{N} \sum_{i=1}^{N} \left[ \frac{V_a^{\exp}(P_i) - V_a(P_i)}{V_a^{\exp}(P_i)} \right]^2 \right)^{1/2}
$$

(2.15)

The choice of model isotherm function from which $\theta_m(P,U)$ is determined may be guided by experimental conditions or an arbitrary choice made. The isotherm functions utilised in this investigation have been discussed in Section 2.2.

It is possible to propose general forms for $F'(U)$, e.g. Gaussian distribution (Ross and Olivier, 1964), exponential distribution (Steele, 1974) and by adjustment of variable parameters by numerical optimisation methods or graphical techniques (Adamson and Ling, 1961), the method usually attempted, to determine the 'best-fit' of $F'(U)$. This method suffers from the limitation imposed by the
choice of the generalised form of \( F'(U) \). It is far less restrictive
to determine \( F(U) \) or \( F'(U) \) without any presupposition of a
distribution function.

2.3.2. Normalisation of \( F'(U) \)

If some initial approximation to \( F'(U) \) can be established to that
\( F'(U) \) is normalised and consequently the maximum value of \( F(U) = 1 \),
then equation 2.14 may be rewritten:

\[
V_a(P)_l = V_m \int_0^1 \theta(P,U)dF(U) \\
V_a(P)_n = V_m \int_0^1 \theta(P,U)dF(U)
\]

(2.16)

In a hypothetical situation when no multilayer adsorption can
occur, a pressure \( P_m \) exist at which monolayer coverage is
complete. In this instance \( \theta_m(P_m,U) = 1 \) for all values of \( U \),
and from equation 2.16:

\[
V_a(P_m) = V_m
\]

(2.17)

Hence \( V_m \) corresponds to the monolayer capacity of the surface. In
less ideal circumstances, e.g. when substantial multilayer adsorption
occurs before the completion of the monolayer, \( V_m \) has little
physical significance and is referred to as the normalising capacity.
2.3.3. Initial Approximation of $F'(U)$

The initial determination of $F(U)$ may be guided by reference to the isotherm model at near or below the critical temperature of the adsorbed phase (see Section 2.2.1).

Adopting equation 2.16 yields $F(U_j)$:

$$F(U_j) = \int_0^1 \frac{dF(U)}{dF(U)} + \int_0^{F(U_j)} 1.dF(U)$$

hence:

$$\frac{V_a(P_j)}{V_m} = F(U_j)$$

which may be evaluated from the condition:

$$\frac{V_a(P_N)}{V_N} = 1 \rightarrow F(U_N) = 1$$

2.3.4. Iterative Method

If this approximation to $F(U)$ is used in equation 2.16, then $\Theta_m(P,U)$ has to be determined by an iterative method from the model isotherm equation presented in Section 2.2. This makes the evaluation of the integrals in equation 2.16 in the form:

$$V_a(P_j) = V_m \int_0^1 F(U)d\Theta_m(P_j,U)$$

$$V_a(P_N) = V_m \int_0^1 1$$
and in contrast to equation 2.14, the distribution is of finite width as determined by the limiting pressures \( P_1 \) and \( P_N \). From equation 2.20, the integral limits will be determined by \( U_1 \) and \( U_N \) and the pressure \( P_j \). If there are any patches of adsorptive energies greater than \( U_1 \), they are assumed to be full, which avoids the difficulty of approximating some adsorptive energy distribution between \( U_1 \) and \( \infty \). 'Patches' of adsorptive energy < \( U_N \) are assumed to be empty. Hence the term in equation 2.20 becomes:

\[
\frac{V_a(P_j)}{V_m} = \frac{\theta_{\text{h}}(P_j)}{\theta_{\text{l}}(P_j)} \int P(U) d\theta(P_j, U) + P(U_1) \times (1 - \theta_{\text{h}}(P_j)) + P(U_N) \theta_{\text{l}}(P_j)
\]

(2.21)

This equation may be used to determine r.m.s. and the iterative improvement of \( F(U) \) accomplished from:

\[
F'(U_j) = F^{c-1}(U_j) \frac{V_a^{\text{exp}}(P_j)}{V_a(P_j)}
\]

(2.22)

subject to the condition that if:

\[
F^c(U_{j+1}) < F^c(U_j)
\]

then

\[
F^c(U_{j+1}) = F^c(U_j) + 10^{-6}
\]

(2.23)
where the subscript $c$ labels the interaction number. It is also necessary to ensure that $F'(U)$ is normalised by the adjustment of $V_m$ and $F(U)$:

$$V_m^c (U_{j-1}) < F^c (U_j)$$

$$F^c(U_j) = \frac{F^{c-1}(U_{j-1})}{F^{c-1}(U_N)}$$

(2.24)

Once the r.m.s. has reached a minimum, the adsorptive energy distribution function, $F'(U)$, may be derived numerically from $F(U)$.

For a rapid convergence, using this procedure the choice of the initial $F(U)$ is important. The method of Adamson and Ling (1961) chooses the amount adsorbed at monolayer coverage from a BET analysis, $V_m^{(BET)}$ and determines the first approximation to $F(U)$ through:

$$F^1(U_j) = \frac{V_a}{V_m^{(BET)}}$$

(2.25)

This method suffers from the disadvantage that $V_m^{(BET)}$ is not always known or reliable and that the subsequent distribution function, $F'(U)$, is not normalised (i.e. $F(U_N) = 1$). The normalising procedure used here allows an arbitrary choice of $V_m$ which is adjusted in subsequent cycles to give $F(U_N) = 1$. The initial approximation adopted was:

$$F^1(U_j) = \frac{V_a}{V_N}$$

$$V_m = V_N$$

(2.26)
The algorithm used in HILDA represents the $F(U)$ and $F'(U)$ points by cubic splines (House, 1975). Facilities are available for smoothing the data and making multilayer adsorption correction i.e.

$$v'_{a\text{new}} = v'_{a\text{old}} \times (1 - P/P_O) \quad (2.26)$$

where $P_O$ is the saturation vapour pressure of the adsorbate. This has been used by Adamson and Ling (1961) and House et al. (1982) but is a rather arbitrary choice, without clear theoretical foundations.

2.3.5. **Smoothing**

This type of iterative analysis requires highly accurate adsorption isotherms with minimal scatter of the experimental points, as the energy distribution is highly sensitive to small changes in the isotherm. The stability of the distribution function is dealt with in Chapter 4. The first step in the analysis is to reduce the scatter of the experimental points. This is achieved using an $n$-point ($n$ is odd) least-squares quadratic fit to give points lying on the smooth curve which passes through the raw data. The smoothing routine considers the first $n$ points (1 to $n$), finds the best quadratic curve through the points and calculates one fitted point. It continues by considering points 2 to ($n + 1$), 3 to ($n + 2$) etc. until it has covered the whole adsorption isotherm. A smoothing factor, $SM1$, indicates the quality of smoothing. Great care was taken to confirm that the smoothed curve provided a satisfactory curve of best fit to the original raw data of the adsorption isotherm by using a graphic routine called MULTPLOT.
This plotting routine enables the raw data points to be plotted with the smooth curve on the same graph. The graph may be plotted at many pressure ranges. This gives additional support that the smoothed data is the same as the experimental data for the adsorption isotherm. A second smoothing option performs the above operation on the energy distribution function between iterations. The quality of smoothing is reflected in the final iteration (SM2).

The listing of the HILDA program used in this study is given in the Ph.D thesis of House (1975).

2.4. Iterative Method of CAEDMON

This method by Sacher and Morrison (1979) replaces equation 2.1 by the summation:

$$V_a(P_i) = \sum_{j=1}^{N_p} \Sigma_j f(P_i K_j)$$  \hspace{1cm} (2.27)

where $\Sigma_j$ is the surface area of the jth patch, $N_p$ is the number of patches and $f(P_i K_j)$ is the number of moles adsorbed per unit area of patch j at pressure $P_i$. The function $f(PK)$ must be evaluated numerically from the two-dimensional virial equation:

$$\ln P = \ln \frac{1}{A_j} + \frac{2B_{2D}}{A_j} + \frac{3C_{2D}}{A_j^2} + ... - \ln K_j$$  \hspace{1cm} (2.28)

where $A_j$ is the area per adsorbate molecule, $B_{2D}$ and $C_{2D}$ are the two-dimensional reduced virial coefficients.

The problem is posed as the solution of $N$ simultaneous equations of the form of equation 2.27 with $2N_p$ unknowns, i.e the values of $K_j$ and $\Sigma_j$ for each patch. The values of $K_j$ is determined from the step function at the phase transition of the local
isotherm, as does the HILDA method. This leaves \( N \) unknowns, i.e \( \Sigma_i \) and \( N \) simultaneous equations. The optimisation procedure of Lawson and Hanson (1974) is used to determine the set of non-negative values of \( \Sigma_i \) that produces the best agreement between the experimental data and the computed isotherm. The r.m.s. is calculated as in equation 2.15. For nitrogen, the reduced two-dimensional virial coefficients were obtained at 78K from the Tables of Morrison and Ross (1973), i.e. \( B_{2D} = -1.875 \) and \( C_{2D} = 3.369 \), which were used in this study.

2.5. The BET Method

In 1938 Brunauer, Emmett and Teller extended the ideal localised monolayer concept into a multilayer adsorption theory, now known as the BET theory. The 'simple' or '\( \infty \)-form' of the BET equation is:

\[
\frac{x}{V_m(1-x)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \cdot x
\]  

(2.29)

where \( x \) is the relative pressure \( (P/P_0) \), \( V_m \) is the adsorbed amount in a complete ideal localised monolayer and

\[
C = \exp \left[ \frac{(E_1 - E_L)}{RT} \right]
\]  

(2.30)

The term \( E_1 - E_L \) is the difference between the heat of adsorption in the first layer \( (E_1) \) and the heat of liquefaction \( (E_L) \), is known as the 'net' heat of adsorption. Thus from the BET equation the surface area and the approximate heat of adsorption of the solid can be calculated.

For a great many cases of adsorption data, a reasonable straight
line results if \( x/V_a (1-x) \) be plotted against \( x \), in the range \( x = 0.05 \) to \( 0.35 \). The value of \( V_m \) and \( C \) can be calculated from the slope and intercept. The specific surface area, \( S \), in square metres per gram is given by the following expression:

\[
S = V_m N \sigma_0 \times 10^{-21}
\]

where \( N \) is the Avogadro's number and \( \sigma_0 \) is the molecular cross-sectional area of the adsorbate in \( \text{nm}^2 \text{molec}^{-1} \).

2.5.1 Limitations of the BET Theory

The assumptions in the BET theory have been criticised by Young and Crowell (1962) and Gregg and Sing (1967) on the following grounds:

(i) The model assumes that the surface is energetically uniform.
(ii) The model neglects lateral interactions of the adsorbate molecules.
(iii) The molecules in all the adsorbed layers after the first are treated as completely equal.
(iv) A further postulate made at arriving at the BET equation is that the number of adsorbed layers become infinite when the saturated vapour pressure is reached.

While these limitations are well known, the BET model is still used by many workers for the estimation of specific surface area of solids. A body of useful, if empiric data, has been built up, and provides a ranking of surface areas, especially within a particular class of materials.
CHAPTER 3

EXPERIMENTAL
3.1. **Preparation of barium sulphate**

A batch of barium hydroxide was prepared which was carbonate, strontium and calcium free. The following method was used:

500 g of Analar barium chloride (Hopkins and Williams) was dissolved in 1 dm$^3$ of distilled water (triple distilled using permanganate) at 333K. Fitted to the flask was a lime guard-tube, the solution was maintained at 333K in a water bath for 20 hours.

200 g of Analar sodium hydroxide pellets (Hopkins and Williams) were quickly washed in distilled water to remove the surface carbonate, then dissolved in 250 cm$^3$ of distilled water, with the exclusion of carbon dioxide. A clear solution resulted.

Sodium hydroxide solution was added dropwise from a separating funnel to the barium chloride solution, with continuous stirring at 333K, and the mixture was left for 20 hours:

$$\text{BaCl}_2 + 2\text{NaOH} \rightarrow \text{Ba(OH)}_2 + 2\text{NaCl}.$$  

Barium hydroxide solution was ice-cooled then filtered off under nitrogen. The filtrate was washed with 500 cm$^3$ of distilled water. The solid was redissolved in 1 dm$^3$ of boiling water and left to crystallise overnight. This was repeated once more. The solid was dried in a vacuum oven at 298K for 20 hours. 440 g of barium hydroxide was obtained.
440 g of barium hydroxide was dissolved in 850 cm$^3$ of distilled water, then filtered through a filter paper (542 Whatman). The filtrate was placed into a reaction vessel.

112 g of concentrated sulphuric acid (98%, N$_2$ free, 1.84 g H$_2$SO$_4$ $\equiv$ 1 cm$^3$ of H$_2$O) was made up to 300 cm$^3$ with distilled water. Sulphuric acid was added dropwise from a separating funnel into the reaction vessel containing boiling barium hydroxide solution over four hours with continuous stirring. The barium sulphate formed was left in the mother-liquor at 353K in a water bath for 20 hours. The pH of the solution was found to be between 1-2 as shown by indicator paper:

\[
\text{Ba(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 (s) + 2\text{H}_2\text{O}.
\]

(excess)

The supernatant was changed with distilled water every 24 hours for the first five days. The sample was kept in a water bath at 368K. The supernatant was changed, replacing with distilled water, every seven days, for 6 weeks.

The supernatant was decanted, the barium sulphate precipitate was filtered through a Buchner funnel. The sample was placed into a beaker and left to dry in a vacuum oven at 298K for a week. 200 g of barium sulphate was obtained. This barium sulphate sample was labelled sample 1. Another sample of barium sulphate, sample 4, was prepared at Unilever Research, Port Sunlight, using the same procedure.
3.2. X-Ray diffraction

The crystal structure of barium sulphate, sample 1 was studied by X-ray diffraction. A Phillips X-ray diffractometer which produces CuKα radiation was used in conjunction with a Guinier powder X-ray camera. From the X-ray diffraction pattern, Fig. 3.1, the d-lines were calculated using the Bragg equation. The d-lines and intensity for sample 1 were compared to those obtained by Colville and Staudhammer (1967), who used synthetic barium sulphate, see Table 3.1. The values of d-lines and intensity are very similar to those reported by Colville and Staudhammer, which gives very strong support to sample 1 having a orthorhombic unit cell structure.

3.3. Adsorption of STPP onto barium sulphate

3.3.1. Analytical procedure

The adsorption of STPP onto barium sulphate, sample 1, was determined by the depletion of STPP in solution, using the method of Murphy and Riley (1958), better known as the Molybdenum Blue method. This method involves the breakdown of polyphosphate to orthophosphate in acidic conditions, in the presence of molybdate ions, to produce molybdophosphonic acid (phosphomolybdic acid). The molybdophosphonic acid is reduced by hydrazine sulphate to produce a blue colour of uncertain composition.

The intensity of the blue colour is proportional to the amount of phosphate initially incorporated in the heteropoly acid (molybdophosphonic acid), which exhibits maximum absorbance at 820 to 830 nm. Therefore, using this method, a calibration curve may be
Fig. 3.1 Powder diffraction pattern of barium sulphate (sample 1)
TABLE 3.1: Comparison of powder x-ray diffraction pattern of barium sulphate 1 with the published pattern

Instrument: Philips x-ray diffractometer
Source of the x-ray: Cuk
Wave length: 0.15418 nm

<table>
<thead>
<tr>
<th>2θ</th>
<th>d_{obs}/nm</th>
<th>(I/I_1)_{obs}</th>
<th>d_{Ref}/nm</th>
<th>(I/I_1)_{Ref}</th>
</tr>
</thead>
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<td>29</td>
<td>0.4440</td>
<td>16</td>
</tr>
<tr>
<td>20.480</td>
<td>0.4336</td>
<td>29</td>
<td>0.4339</td>
<td>30</td>
</tr>
<tr>
<td>22.823</td>
<td>0.3896</td>
<td>43</td>
<td>0.3899</td>
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<td>23.538</td>
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<td>0.3773</td>
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<td>24.884</td>
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<td>0.3577</td>
<td>30</td>
</tr>
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<td>25.882</td>
<td>0.3442</td>
<td>100</td>
<td>0.3445</td>
<td>100</td>
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<td>26.870</td>
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<td>0.3319</td>
<td>70</td>
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<td>96</td>
<td>0.3103</td>
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<td>0.2482</td>
<td>13</td>
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<tr>
<td>38.775</td>
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<td>14</td>
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<td>6</td>
<td>0.2305</td>
<td>6</td>
</tr>
<tr>
<td>39.506</td>
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<td>10</td>
<td>0.2282</td>
<td>8</td>
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<tr>
<td>40.840</td>
<td>0.2210</td>
<td>21</td>
<td>0.2211</td>
<td>25</td>
</tr>
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<td>0.2121</td>
<td>78</td>
<td>0.2121</td>
<td>80</td>
</tr>
<tr>
<td>42.969</td>
<td>0.2105</td>
<td>63</td>
<td>0.2106</td>
<td>75</td>
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<tr>
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<td>24</td>
<td>0.2057</td>
<td>19</td>
</tr>
<tr>
<td>47.048</td>
<td>0.1931</td>
<td>8</td>
<td>0.1937</td>
<td>7</td>
</tr>
<tr>
<td>49.039</td>
<td>0.1858</td>
<td>20</td>
<td>0.1858</td>
<td>18</td>
</tr>
<tr>
<td>51.045</td>
<td>0.1789</td>
<td>4</td>
<td>0.1789</td>
<td>4</td>
</tr>
<tr>
<td>51.968</td>
<td>0.1759</td>
<td>8</td>
<td>0.1758</td>
<td>10</td>
</tr>
<tr>
<td>53.062</td>
<td>0.1726</td>
<td>6</td>
<td>0.1724</td>
<td>5</td>
</tr>
<tr>
<td>54.839</td>
<td>0.1674</td>
<td>14</td>
<td>0.1674</td>
<td>14</td>
</tr>
<tr>
<td>56.166</td>
<td>0.1638</td>
<td>7</td>
<td>0.1638</td>
<td>8</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$d_{obs}/\text{nm}$</td>
<td>$(I/I_1)_{obs}$</td>
<td>$d_{ref}/\text{nm}$</td>
<td>$(I/I_1)_{ref}$</td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
<td>-----------------</td>
<td>-------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>57.889</td>
<td>0.1593</td>
<td>7</td>
<td>0.1594</td>
<td>8</td>
</tr>
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<td>60.255</td>
<td>0.1536</td>
<td>12</td>
<td>0.1535</td>
<td>15</td>
</tr>
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<td>60.569</td>
<td>0.1529</td>
<td>10</td>
<td>0.1527</td>
<td>8</td>
</tr>
<tr>
<td>62.994</td>
<td>0.1475</td>
<td>11</td>
<td>0.1475</td>
<td>10</td>
</tr>
</tbody>
</table>
constructed of absorbance versus concentration of STPP which is used to obtain the concentration of STPP which is used to obtain the concentration of free STPP in an equilibrated solution of barium sulphate and STPP.

This method only works if there is an absence of silicate, arsenate, germanate and tungstate: also lead, antimony and copper are known to interfere.

3.3.1.1. Reagents

Molybdate solution was prepared by dissolving 12.5 g of Analar reagent of sodium molybdate (Na$_2$MoO$_4$•2H$_2$O) in 500 cm$^3$ of 5M sulphuric acid.

Hydrazinium sulphate solution was prepared by dissolving 1.5 g of Analar reagent of hydrazinium sulphate in 1 dm$^3$ of distilled water.

Standard polyphosphate solution (10$^{-3}$M) was prepared by dissolving 0.476 g of STPP (prepared at Port Sunlight Laboratories) in 1 dm$^3$ of distilled water.

3.3.1.2. Construction of calibration curve

Solutions of STPP were made within the concentration range 10$^{-6}$ to 10$^{-5}$M from the standard polyphosphate solution. To each 10 cm$^3$ of STPP solution was added 5 cm$^3$ of molybdate solution and 2 cm$^3$ of hydrazinium sulphate solution. This was then diluted to 20 cm$^3$ with triple distilled water and shaken vigorously. The solutions were placed into a boiling water batch for 10 minutes, removed and cooled rapidly.
The solution (blue in colour) was pipetted into a quartz cuvette and placed into a spectrophotometer (Perkin-Elmer Coleman 55 single scan). The absorbance at 826 nm was measured for each solution against distilled water as the blank.

The calibration curve obtained is shown in Fig. 3.2. The extinction coefficient calculated from the calibration curve is 1772 m$^2$/mol$^{-1}$, which is similar to the extinction coefficient obtained by R Smith (1982).

### 3.3.2. Adsorption of STPP onto barium sulphate at neutral pH

Solutions of STPP were made with a concentration range from $2 \times 10^{-6}$ to $5 \times 10^{-4}$ M. To each 10 cm$^3$ of STPP solution was added 0.02 g of sample 1. The samples were placed on a end-over-end rotator for 24 hours for equilibrium to be established. Sample 1 with adsorbed STPP from each solution was removed using a 0.2 μm millipore filter under nitrogen. These samples were dried at room temperature and were stored for ESCA analysis.

The pH of the solutions were measured with a pH meter. The amount of STPP remaining in solution (or equilibrium concentration) was determined by the Molybdenum Blue method described above. However, for some solutions a very intense blue colour were obtained. These solutions were diluted with distilled water by a factor of 2 to 10, thus enabling an absorbance to be determined by the spectrophotometer within the calibration range. The dilution factors were taken into account in the calculations (Table 3.2). The solution adsorption isotherm of STPP on sample 1 at neutral pH is shown in Fig. 3.3.
Fig. 3.2 Calibration curve of STPP concentration versus absorbance at 826nm
<table>
<thead>
<tr>
<th>Initial concentration of STP (moldm$^{-3}$)</th>
<th>Weight of BaSO$_4$ (2 g)</th>
<th>Absorbance at 826 nm</th>
<th>Equilibrium concentration of STP (moldm$^{-3}$)</th>
<th>Amount of STP adsorbed (molg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 10^{-6}$</td>
<td>0.0211</td>
<td>0.022</td>
<td>$0.100 \times 10^{-6}$</td>
<td>$9.0047 \times 10^{-7}$</td>
<td>7.50</td>
</tr>
<tr>
<td>$4 \times 10^{-6}$</td>
<td>0.0203</td>
<td>0.023</td>
<td>$0.100 \times 10^{-6}$</td>
<td>$1.9212 \times 10^{-6}$</td>
<td>7.62</td>
</tr>
<tr>
<td>$6 \times 10^{-6}$</td>
<td>0.0213</td>
<td>0.050</td>
<td>$0.600 \times 10^{-6}$</td>
<td>$2.5352 \times 10^{-6}$</td>
<td>-</td>
</tr>
<tr>
<td>$8 \times 10^{-6}$</td>
<td>0.0212</td>
<td>0.047</td>
<td>$0.550 \times 10^{-6}$</td>
<td>$3.5142 \times 10^{-6}$</td>
<td>-</td>
</tr>
<tr>
<td>$1 \times 10^{-5}$</td>
<td>0.0207</td>
<td>0.079</td>
<td>$1.100 \times 10^{-6}$</td>
<td>$4.2995 \times 10^{-6}$</td>
<td>7.74</td>
</tr>
<tr>
<td>$2 \times 10^{-5}$</td>
<td>0.0207</td>
<td>0.103</td>
<td>$1.500 \times 10^{-6}$</td>
<td>$8.9372 \times 10^{-6}$</td>
<td>7.72</td>
</tr>
<tr>
<td>$4 \times 10^{-5}$</td>
<td>0.0205</td>
<td>0.457</td>
<td>$7.925 \times 10^{-6}$</td>
<td>$1.5646 \times 10^{-5}$</td>
<td>7.45</td>
</tr>
<tr>
<td>$6 \times 10^{-5}$</td>
<td>0.0216</td>
<td>0.922</td>
<td>$1.595 \times 10^{-5}$</td>
<td>$2.0394 \times 10^{-5}$</td>
<td>-</td>
</tr>
<tr>
<td>$8 \times 10^{-5}$</td>
<td>0.0212</td>
<td>0.347 (diluted 5x)</td>
<td>$2.975 \times 10^{-5}$</td>
<td>$2.3703 \times 10^{-5}$</td>
<td>7.66</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>0.0207</td>
<td>0.584 (diluted 5x)</td>
<td>$5.100 \times 10^{-5}$</td>
<td>$2.3703 \times 10^{-5}$</td>
<td>7.63</td>
</tr>
</tbody>
</table>
The above procedure was repeated, except the solution adsorption isotherm was determined at pH 9.0 (see Table 3.3). The solution adsorption isotherm is shown in Fig. 3.3.

3.3.2.1. General considerations

The solution adsorption isotherm of STPP on barium sulphate, sample 1, at neutral pH was utilised to prepare two samples with a known coverage of STPP on the surface of sample 1. These samples were used for gas adsorption studies at liquid nitrogen temperatures.

From Fig. 3.3, the plateau region (at $2.4 \times 10^{-5}$ moles of STPP adsorbed per gram of sample 1) indicates the monolayer coverage of STPP on the surface of sample 1 at pH 7.6. To prepare a sample below the monolayer coverage, the initial sharp rise of the solution isotherm was considered. However, due to large errors at low equilibrium concentration of STPP, preparation of a sample with known coverage under these conditions was not feasible. Hence a 38% monolayer coverage of adsorbed STPP on sample 1 was chosen i.e. at an adsorbed amount of $9 \times 10^{-6}$ mol g$^{-1}$.

The error in the STPP coverage at the monolayer (i.e. 100% STPP coverage) and fractional monolayer (i.e. 38% STPP coverage) samples in this work was estimated from the solution adsorption isotherm at neutral pH to be $\pm 5\%$ and $\pm 10\%$, respectively.

For this study two samples were prepared, one at monolayer coverage and the other below monolayer coverage. The preparative details are given below.
Fig. 3.3 Solution adsorption isotherm of STPP onto sample 1 at 295K

Equilibrium concentration of STPP (mmoldm$^{-3}$)
TABLE 3.3: Solution adsorption isotherm data for STPP onto sample 1 at pH 9.0 at 295K

<table>
<thead>
<tr>
<th>Initial concentration of STP (mol dm⁻³)</th>
<th>Weight of BaSO₄ ₂ (g)</th>
<th>Absorbance at 826 nm</th>
<th>Equilibrium concentration of STP (mol dm⁻³)</th>
<th>Amount of STP adsorbed (mol g⁻¹)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 x 10⁻⁶</td>
<td>0.0202</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.66</td>
</tr>
<tr>
<td>8 x 10⁻⁶</td>
<td>0.0204</td>
<td>0.024</td>
<td>1.000 x 10⁻⁷</td>
<td>3.8725 x 10⁻⁶</td>
<td>8.21</td>
</tr>
<tr>
<td>1 x 10⁻⁵</td>
<td>0.0205</td>
<td>0.038</td>
<td>3.700 x 10⁻⁷</td>
<td>4.6976 x 10⁻⁶</td>
<td>8.83</td>
</tr>
<tr>
<td>2 x 10⁻⁵</td>
<td>0.0202</td>
<td>0.044</td>
<td>4.750 x 10⁻⁷</td>
<td>9.6658 x 10⁻⁶</td>
<td>9.45</td>
</tr>
<tr>
<td>6 x 10⁻⁵</td>
<td>0.0208</td>
<td>0.119</td>
<td>1.840 x 10⁻⁶</td>
<td>2.7962 x 10⁻⁵</td>
<td>9.03</td>
</tr>
<tr>
<td>8 x 10⁻⁵</td>
<td>0.0214</td>
<td>0.586 (diluted 2x)</td>
<td>2.050 x 10⁻⁵</td>
<td>2.7804 x 10⁻⁵</td>
<td>8.89</td>
</tr>
<tr>
<td>1 x 10⁻⁴</td>
<td>0.0209</td>
<td>0.309 (diluted 5x)</td>
<td>2.625 x 10⁻⁵</td>
<td>3.5285 x 10⁻⁵</td>
<td>9.22</td>
</tr>
<tr>
<td>2 x 10⁻⁴</td>
<td>0.0200</td>
<td>0.214 (diluted 10x)</td>
<td>3.550 x 10⁻⁵</td>
<td>8.2250 x 10⁻⁵</td>
<td>9.45</td>
</tr>
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</table>
3.3.2.2. **Monolayer coverage sample**

From the solution adsorption isotherm, Fig. 3.3, we see that in order to prepare monolayer coverage of adsorbed STPP on sample 1 at pH 7.6, an STPP equilibrium concentration of > 5 x 10^{-5} M is required. This was obtained with 10 cm$^3$ of 10^{-4} M STPP solution with 0.02 g of sample 1. Additional STPP may go down during drying, however filtering reduces the amount of STPP available. The samples are labelled according to the amount of STPP adsorbed in solution. It would be interesting to quantify the amount of STPP on the dried samples however, this is not important for this study where we seek to detect changes in the energy distribution due to near monolayer and sub-monolayer amounts.

To prepare this sample in bulk, the procedure was as follows:

0.6 g of sample 1 was added to 300 cm$^3$ of 10^{-4} M STPP solution in a standard flask. The flask was placed onto an end-over-end rotator for 24 hours for equilibrium to be established. Sample 1 with adsorbed STPP was filtered with a 0.2 μm millipore filter under nitrogen. The sample was dried at room temperature. This sample was labelled as sample 3 with a 100% monolayer coverage of STPP on sample 1.

3.3.2.3. **Fractional monolayer coverage sample**

Again from Fig. 3.3, we see that the preparation of a 38% monolayer coverage of STPP on sample 1 at pH 7.6, requires an STPP equilibrium concentration of 1.5 x 10^{-6} M. This was obtained from 10 cm$^3$ of 2 x 10^{-5} M STPP solution with 0.02 g of sample.
To prepare this sample in bulk, the procedure was as follows:

0.6 g of sample 1 was added to 300 cm$^3$ of 2 x $10^{-5}$ M STPP solution in a standard flask. The procedure is followed as in Section 3.3.2.2. This sample was labelled sample 2 with a 38% monolayer coverage of STPP on sample 1.

Both the above samples were used for gas adsorption studies at liquid nitrogen temperatures and also studied under an scanning electron microscope.

### 3.3.3. Discussion

The adsorption of STPP on barium sulphate was studied in the solution phase at pH 7.6 and the adsorption isotherm was found to be of a Langmuir type for the concentration range studied. Similar results were obtained by Smith (1982) for barium sulphate and by Miura et al. (1966) for strontium sulphate. The latter investigation showed an increase in adsorption of STPP at higher pH; this effect was demonstrated in this study of barium sulphate by the determination of the solution adsorption isotherm at pH 9.0.

### 3.4. Scanning electron microscopy

To study the surface topology of samples 1, 2, 3 and 4, a scanning electron microscope (JSM35 from JEOL Ltd) was utilised.

To produce a high intensity of secondary electrons, the samples were coated with a thin layer of carbon under vacuum, then coated with a thick layer (100 nm) of gold under vacuum. The electron micrographs are shown in Figs. 3.4, 3.5, 3.6, 3.7 and 3.8.
Fig. 3.4 Electronmicrograph of sample 4 (Mag. X6,000)

Fig. 3.5 Electronmicrograph of sample 1 (Mag. X20,000)
Fig. 3.6 Electronmicrograph of sample 2 (Mag. X60)
Fig. 3.7 Electronmicrograph of sample 2 (Mag. X30,000)

Fig. 3.8 Electronmicrograph of sample 3 (Mag. X45,000)
**TABLE 3.4. Particle length range estimated from the electronmicrographs**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>FIGURE</th>
<th>Particle length range $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>0.5 – 0.2</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>200 (spherulite)</td>
</tr>
<tr>
<td>2</td>
<td>3.7</td>
<td>0.7 – 0.2</td>
</tr>
<tr>
<td>3</td>
<td>3.8</td>
<td>0.7 – 0.2</td>
</tr>
<tr>
<td>4</td>
<td>3.4</td>
<td>2.6 – 0.75</td>
</tr>
</tbody>
</table>
Fig. 3.4 shows the electron micrograph of sample 4, which was in a powdered form. The particle shape of the barium sulphate crystals are variable and aggregated together. The size of the particles vary considerably. Steps, edges on the crystal surfaces of barium sulphate can be seen on the large particles.

Fig. 3.5 shows the electron micrograph of sample 1. The clarity of this electron micrograph was poor since the focussing on very small particles was extremely difficult. This was also the case for sample 2 and 3 see Figs. 3.7 and 3.8 respectively. The general shape and size of particles for samples 1, 2 and 3 was variable. Sample 2 was in the form of spherulites (i.e agglomeration of small particles in the form of a sphere (see Fig. 3.6)). A closer inspection of a spherulite is shown in Fig. 3.7.

Table 3.4 shows the estimated particle length range for each sample. Sample 4 has 3 to 4 times the particle length compared to sample 1, 2 and 3. The adsorption of STPP has not changed the particle length of barium sulphate.

3.4.1. Discussion

The electron micrographs show that the particle size and shape of barium sulphate varied, and that the particles are small aggregates as has previously been observed by Jopling (1952) and Kilthoff and MacNevin (1937). The electron micrograph of sample 4 clearly shows that this sample has a larger particle size than sample 1 and that
surface defects are present on some of the particles. It may be this type of defect which gives rise to high energy sites on the surface of crystals.

van Rosmalen and van der Leeden (1982), and Leung and Nancollas (1978) have suggested that defects on the surface of barium sulphate are the growth sites controlling the formation of the precipitate. Nancollas (1968) has suggested that a sufficient number of growth sites must be provided initially for crystal growth to occur. Investigations of the role of growth sites have involved various inhibitors or additives such as metal ions, polyphosphates and phosphonates in adsorption and kinetic studies [Koutsoukos et al. (1981), van Rosmalen (1980), van Rosmalen and van der Leeden (1982), Hiura et al. (1963), Rizkalla (1983) and Smith (1982)].

Sample 2 was in the form of spherulites and these have also been observed by Miura (1963) for strontium sulphate/phosphate system and by Smith and Puddington (1960) for barium sulphate/organic media. The latter authors suggest that a small quantity of water is necessary for this phenomena to occur.

However, sample 3 was in the form of a powder. Examination of the two samples by scanning electron microscope show that the particles for sample 2 are aggregated more than for sample 3. The particles vary in shape and size.
3.5. **Electron spectroscopy for chemical analysis (ESCA)**

ESCA determines the binding energies of electrons in the various electronic energy levels of an atom, ion or molecule. Orbital binding energies, or ionisation potentials are characteristic features of the parent species and can therefore be used for their identification and quantification.

The Vacuum-Generators ESCA3 spectrometer was used for this study, which utilises a monoenergetic beam of soft X-ray (AlKα energy 1487 eV) as an ionising source. Photoelectrons ejected from the various energy levels of the atoms or ions comprising of the sample pass into an electrostatic analyser which determines the number of photoelectrons as a function of kinetic energy. Electrons released from particular energy levels occur at peaks in the spectrum. A small quantity of gold evaporated onto the sample provides a reference peak of known binding energy.

A photoelectron generated within the sample can contribute to its characteristic peak, if it reaches the surface without energy loss, i.e. by inelastic scattering. For typical photoelectron energies, up to 1500 eV, the electron mean free path for inelastic scattering is of the order of 1-5 nm. This determines that only the outermost 5 nm or so of the solid contributes to the photoelectron spectrum. Relative peak heights are translated into relative numbers of atoms or ions in a surface by the use of elemental sensitivity factors.

To apply ESCA to the study of adsorption of STPP on barium sulphate (sample 1), the crystals were removed from suspensions by filtration through a 0.2 μm millipore filter and dried at room temperature.
A small section (approximately 1 cm$^2$) of the filter with adhering crystals was mounted on the sample probe of the spectrometer.

3.5.1. Result and Discussion

From the electron spectrum obtained, surface Ba to adsorbate ratios were calculated using relative peak heights and applying the sensitivity factors of Jorgensen and Berthov (1973), (see Table 3.5). Table 3.6 shows the ratios of the atomic ratios of the elements present at the surface of these presorbed samples. Column 2, 3 and 4 show the ratio of the Ba, S and O atoms of the presorbed samples compared with the bare surface of barium sulphate. These results have been plotted in Fig. 3.9. The results show that the phosphorus atoms qualitatively follow the same curve as the solution adsorption isotherm. Also, the sulphur and oxygen atoms follow the same trend.

Columns 6, 7 and 8 in Table 3.6 show the ratios of sulphur, oxygen and phosphorus to that of barium are the same. The results are shown in Fig. 3.10. The results indicate that sulphur and oxygen atoms decrease with concentration but phosphorus atoms increase with concentration. This would suggest that the sulphate group is being exchanged for the phosphate group on the surface of barium sulphate. Rizkalla (1983) has suggested that adsorption of additives such as STPP may be attributed to the simultaneous chelation of an active site metal ion and adsorption on the surface through a phosphonate/sulphate exchange.

The carbon was from the filter paper on which the samples were placed.
TABLE 3.5: ESCA results for barium sulphate 1 with preadsorbed STPP at pH 7.6

<table>
<thead>
<tr>
<th>Equilibrium concentration (mmoldm$^{-3}$)</th>
<th>Sample number</th>
<th>Atomic ratios of elements present at the surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ba</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>19.4</td>
</tr>
<tr>
<td>0.100 x 10$^{-6}$</td>
<td>2</td>
<td>20.3</td>
</tr>
<tr>
<td>0.100 x 10$^{-6}$</td>
<td>3</td>
<td>19.0</td>
</tr>
<tr>
<td>0.600 x 10$^{-6}$</td>
<td>4</td>
<td>19.0</td>
</tr>
<tr>
<td>0.550 x 10$^{-6}$</td>
<td>5</td>
<td>19.7</td>
</tr>
<tr>
<td>1.100 x 10$^{-6}$</td>
<td>6</td>
<td>19.0</td>
</tr>
<tr>
<td>1.500 x 10$^{-6}$</td>
<td>7</td>
<td>19.7</td>
</tr>
<tr>
<td>7.925 x 10$^{-6}$</td>
<td>8</td>
<td>16.0</td>
</tr>
<tr>
<td>1.595 x 10$^{-5}$</td>
<td>9</td>
<td>17.3</td>
</tr>
<tr>
<td>2.975 x 10$^{-5}$</td>
<td>10</td>
<td>17.0</td>
</tr>
<tr>
<td>5.100 x 10$^{-5}$</td>
<td>11</td>
<td>17.3</td>
</tr>
<tr>
<td>Sample number</td>
<td>Ba/Ba₁</td>
<td>S/S₁</td>
</tr>
<tr>
<td>---------------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>1.046</td>
<td>1.047</td>
</tr>
<tr>
<td>3</td>
<td>0.979</td>
<td>0.865</td>
</tr>
<tr>
<td>4</td>
<td>0.979</td>
<td>0.965</td>
</tr>
<tr>
<td>5</td>
<td>1.015</td>
<td>0.982</td>
</tr>
<tr>
<td>6</td>
<td>0.979</td>
<td>0.800</td>
</tr>
<tr>
<td>7</td>
<td>1.015</td>
<td>0.865</td>
</tr>
<tr>
<td>8</td>
<td>0.825</td>
<td>0.676</td>
</tr>
<tr>
<td>9</td>
<td>0.892</td>
<td>0.688</td>
</tr>
<tr>
<td>10</td>
<td>0.876</td>
<td>0.723</td>
</tr>
<tr>
<td>11</td>
<td>0.982</td>
<td>0.771</td>
</tr>
</tbody>
</table>
Fig. 3.9 ESCA results showing the ratio of the component from the adsorbed sample to the pure sample for barium, sulphur, oxygen and phosphorous

Equilibrium concentration of STPP (mmol dm$^{-3}$)
Fig. 3.10 ESCA results plotted as sulphur, oxygen and phosphorous to barium ratio for the STPP adsorption on sample 1 at pH 7.6.
3.6. Adsorption apparatus

In this investigation, a volumetric method was employed to determine gas adsorption isotherms at liquid nitrogen temperatures. The adsorption apparatus used is shown in Figs. 3.11 and 3.12. A simplified schematic representation of the adsorption apparatus is shown in Fig. 3.13.

The pumping system consisted of an Edwards Diffstak with a 63 mm diffusion pump utilising Santovac 5 fluid and a Edwards model EDK2 rotary pump. Two Edwards Pirani gauges were employed: one was incorporated between the rotary and diffusion pumps, the other was placed above the diffusion pump. These were used to measure the backing pressure and were also used for leak detection. An ionisation gauge was included on the main frame of the adsorption apparatus to measure the vacuum of the system and to establish full outgassing of the sample under investigation. A liquid nitrogen trap was incorporated between the pumps and the main working volume.

The main working volume was constructed of Pyrex glass. The taps (represented by crosses in Fig. 3.13) were Springham greaseless vacuum valves with a Viton A diaphragm. A small change in volume (approx. 0.25 cm$^3$) is found when these taps were fully opened and closed. Hence, the number of turns required to open and close the taps was always the same. The adsorption apparatus was free from grease and mercury contamination.

3.6.1. Sample

The sample under investigation was glass-blown onto the adsorption apparatus above the level of the liquid N$_2$/O$_2$ bath.
Fig. 3.11 Adsorption measurement apparatus
Fig. 3.12 Sample region of adsorption measurement apparatus
Fig. 3.13 Schematic representation of the adsorption measurement apparatus
The samples were outgassed at 353K under a vacuum of better than $6 \times 10^{-6}$ mmHg over a period of 60 hours. The sample was allowed to cool to room temperature within the furnace, and then the furnace was removed. To check that the sample was fully outgassed, the tap above the sample was closed and the pressure reading was followed overnight.

The adsorption apparatus was used to measure the experimental adsorption isotherms at low pressure i.e. from $10^{-5}$ to 1 mmHg and high pressure i.e. from $10^{-2}$ to 1000 mmHg.

**Key to Fig. 3.13**

- **PG** - Pirani Gauge
- **IG** - Ionisation Gauge
- **P1** - Capacitance manometer in dosage region with a pressure range: $10^{-4} - 10$ mmHg
- **P2** - Capacitance manometer in sample region with a pressure range: $10^{-5} - 1$ mmHg
- **P3** - Capacitance manometer in dosage region with a pressure range: $10^{-2} - 1000$ mmHg
- **P4** - Capacitance manometer in sample region with a pressure range: $10^{-2} - 1000$ mmHg
- **S1** - Sample for low pressure section
- **S2** - Sample for high pressure section
- **V1cal** - Calibrated volume for low pressure section
- **V2cal** - Calibrated volume for high pressure section
- **VP** - Vapour pressure thermometer
- **TExt** - External tap to bleed air into the apparatus
- **TIC** - Thermally insulated cabinet
- **X** - Springham greaseless vacuum valves with a Viton A diaphragm
3.6.2. Low pressure measurements

The low pressure measurements were carried out in the upper half of the adsorption apparatus, as shown in Fig. 3.13. This consisted of a sample region, which included a sample tube and a capacitance manometer, M.K.S. Baratron type 145 AH-1, with a pressure range from $10^{-5}$ to 1 mmHg. The dosage region had a calibrated volume, enabling the volume of the dosage region to be increased. This bulb was calibrated with triple distilled water at 298.0K and weighed. A capacitance manometer, M.K.S. Baratron type 145 AH-10, with a pressure range from $10^{-4}$ to 10 mmHg was placed above the calibrated volume in the dosage region.

Both of the capacitance manometers have a quoted error maximum of 10% at the low end of the range and 0.08% at the highest pressure on a linear scale. These capacitance manometers were zeroed with the vacuum produced by the pumps i.e better than $10^{-6}$ mmHg. Integral heaters were provided, so that they could be thermostatted at a temperature of 322 ± 0.14K during normal use. The electronic unit type 170M was used to provide power to the capacitance manometers and convert the output to a proportional DC output of ± 10 V DC full scale. The voltage was directly outputted from the control unit to a Solartron model 7050 digital voltmeter.

3.6.3. High pressure measurements

The high pressure measurements were performed by the lower half of the adsorption apparatus, (see Fig. 3.13). The sample and dosage regions were similar to the low pressure sample and dosage region.
However, an absolute capacitance manometer, M.K.S. Baratron type 310 BHS-1000 were used for the sample and dosage regions. The pressure range for these absolute capacitance manometers was from $10^{-2}$ to 1000 mmHg, with a quoted error maximum of 10% at the low end of the range to 0.08% at the highest pressure on a linear scale. These capacitance manometers were zero fixed, but are electrically connected and thermostatted in the same manner as the low pressure capacitance manometers.

3.6.4. Accuracy of Pressure Measurements

To monitor accurately the voltage reading from the capacitance manometers, a chart recorder (Smith) was used, which was made to display the difference between a backing voltage derived from a DC voltage calibrator (Time Electronic Limited - Type 20035). All the voltage readings in this investigation were determined by this method which enabled monitoring of mV differences in voltage readings.

3.6.5. Maintenance of Sample Temperature

To monitor the sample temperature a saturation vapour pressure manometer was included on the adsorption apparatus (see Fig. 3.12). This was filled with either nitrogen or oxygen, such that a small amount would condense in the bulb A and B (Fig. 3.13) when immersed in a mixture of liquid $N_2$ and $O_2$. A magnetic stirrer was used to continually mix the liquid $N_2/O_2$ mixture in the dewar. The level of the liquid $N_2/O_2$ mixture was maintained at a fixed height by small additions of liquid $N_2$ or a mixture of liquid $N_2/O_2$, depending on the temperature of the liquid $N_2/O_2$ bath.
The temperature of the liquid $N_2/O_2$ bath was determined from the difference in height of the mercury level, $\Delta h$, in the manometer as, one side had a vapour pressure produced by the condensed nitrogen or oxygen and the other side was under vacuum, produced by a two stage rotary pump (Edwards model EDM2). The saturation vapour pressure was calculated for nitrogen as follows:

Using the saturation and thermodynamic properties of nitrogen given by Jacobsen (1975), the triple point is at 63.148K, the boiling point at 77.347K at 760 mmHg and the critical point is at 126.2K ($T_c$). The analytical representation of this data is given by:

$$\ln P = \frac{A_1}{T} + A_2 + A_3T + A_4 (T_c - T)^{1.95} + A_5T^3$$

$$+ A_6T^4 + A_7T^5 + A_8T^6 + A_9 \ln(T)$$

The coefficients for this equation ($A_1$ to $A_9$) are given in Table 3.7. The pressure $P$, is in atmospheres, and $T$ is the temperature. This equation was used to determine the saturation vapour pressure of nitrogen at 77.8K.

The saturation vapour pressure of oxygen was calculated using the saturation and thermodynamic properties of oxygen given by Roder et al (1972); the triple point is at 54.351K, the boiling point is at 90.18K, and the critical point is at 154.576K. The analytical representation of this data is given by:

$$\ln P = A_1 + A_2T + A_3T^2 + A_4T^3 + A_5T^4$$

$$+ A_6T^5 + A_7T^6 + A_8T^7$$

(3.2)
The coefficients for this equation \((A_1 \text{ to } A_8)\) are given in Table 3.7. The pressure, \(P\) is in atmospheres, and \(T\) is the temperature. This equation was used to determine the saturation vapour pressure of oxygen at 80.8K and 81.6K.

The difference in height, \(\Delta h\), was calculated from the saturation vapour pressure, \(P\), using the following equation:

\[
P \times 76 = \Delta h \text{ (cm)} \quad (3.3)
\]

<table>
<thead>
<tr>
<th>COEFFICIENT</th>
<th>NITROGEN</th>
<th>OXYGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>(0.839441 \times 10^4)</td>
<td>(-62.5967185)</td>
</tr>
<tr>
<td>(A_2)</td>
<td>(-0.189004 \times 10^4)</td>
<td>(2.47450429)</td>
</tr>
<tr>
<td>(A_3)</td>
<td>(-0.728223 \times 10^1)</td>
<td>(-4.689733 \times 10^{-2})</td>
</tr>
<tr>
<td>(A_4)</td>
<td>(0.102285 \times 10^{-1})</td>
<td>(5.482023 \times 10^{-4})</td>
</tr>
<tr>
<td>(A_5)</td>
<td>(0.555606 \times 10^{-3})</td>
<td>(-4.093498 \times 10^{-6})</td>
</tr>
<tr>
<td>(A_6)</td>
<td>(-0.594454 \times 10^{-5})</td>
<td>(1.914719 \times 10^{-8})</td>
</tr>
<tr>
<td>(A_7)</td>
<td>(0.271543 \times 10^{-7})</td>
<td>(-5.131137 \times 10^{-11})</td>
</tr>
<tr>
<td>(A_8)</td>
<td>(-0.487953 \times 10^{-10})</td>
<td>(6.026569 \times 10^{-14})</td>
</tr>
<tr>
<td>(A_9)</td>
<td>(0.509536 \times 10^3)</td>
<td>(-)</td>
</tr>
</tbody>
</table>

3.6.6. Volume Calibrations

The sample and dosage region volumes were determined for both the low and high pressure regions. The sample region volume (containing the sample) was determined with and without the liquid \(N_2/O_2\) bath. These volumes were required for the calculation of the adsorption isotherm.
A helium expansion method was utilised for two main reasons:

(i) Helium is not significantly adsorbed by the sample at temperatures used in this investigation.

(ii) Helium is a close approximation to an ideal gas.

The procedure to be described is the same for the low and high pressure regions of the adsorption apparatus.

3.6.6.1. Dosage Region

![Diagram]

$T_1, T_2, T_3$ represents taps 1, 2 and 3
$V_c$ is the calibrated volume
$V_d$ is the dosage volume
$V_s$ is the sample volume.

Before the calibration proceeded, the entire working volume was evacuated. Helium was introduced in the volumes $V_d$ and $V_c$. The equilibrium pressure from $P_1$ was recorded e.g. $P_{1_A}$. Tap $T_2$ was closed. The helium in region $V_d$ was evacuated. Tap $T_2$ was
opened, to expand the helium from $V_c$ to $V_c$ and $V_d$. The new equilibrium pressure was recorded from $P_l$ e.g $P_{l_B}$. Since the volume of $V_c$ is known, then $V_d$ may be calculated from the following expression:

$$\frac{V_c (P_{l_A} - P_{l_B})}{P_{l_B}} = V_d$$

(3.4)

This procedure was repeated until consistent results were obtained for $V_d$ at 295K.

3.6.6.2. **Sample Region**

The whole working frame was evacuated. $T_1$ and $T_2$ was closed. Helium was introduced into $V_d$. Tap $T_3$ was closed. The equilibrium pressure was recorded from $P_l$ e.g $P_{l_c}$. $T_1$ was opened and the helium was expanded from $V_d$ to $V_d$ and $V_s$. The new equilibrium pressure on $P_l$ was recorded e.g $P_{l_d}$ (identical pressure readings would be obtained from $P_2$). Since the volume of $V_d$ is known from above, then $V_s$ may be calculated from the following equation:

$$\frac{V_d (P_{l_c} - P_{l_d})}{P_{l_d}} = V_s$$

(volume of the sample region at room temperature)

(3.5)

The above procedure was repeated, although sometimes the $V_c$ and $V_d$ were used together, until consistent results were obtained for $V_s$ at 295K.

The above procedure was adopted when the sample bulb was partially immersed in liquid $N_2/O_2$ mixture, to determine $V_s^C$ (volume of the sample with a liquid $N_2/O_2$ both at a fixed height) at 77.8K.
This calibration procedure was used for each new sample placed onto the apparatus.

3.7. Thermal Transpiration

Thermal transpiration must be taken into account when a sharp thermal junction exists in a system at low pressure. In this investigation, the sample bulb was maintained at 77.8K by a liquid N₂/O₂ bath, the pressure at this temperature is lower than that of the gas in the remainder of the system. Therefore, at low pressure, when the mean free path is very much smaller than the internal diameter of the sample tube, the ratio of the pressure above (Pₐ) and pressure below (Pₐ) the thermal junction is given by the Knudsen equation:

$$\frac{P_a}{P_b} = \left[ \frac{T_a}{T_b} \right]^{1/2} \quad (3.6)$$

where Tₐ and Tₐ are the higher and lower absolute temperatures, respectively.

When the mean free path is not less than the internal diameter of the sample tube other theoretical treatments (Liang, 1953, 1955, 1952, 1951; Weber, 1937 and Mason et. al., 1963) have been used to describe the variation of the ratio Pₐ/Pₐ. Of these, the most widely used is the semi-empirical equation proposed by Liang (1955):

$$R_g = \frac{P_a}{P_b} = \frac{\alpha_{He}(\Theta \ x)^2 + \beta_{He}(\Theta \ x) + R_m}{\alpha_{He}(\Theta \ x)^2 + \beta_{He}(\Theta \ x) + 1} \quad (3.7)$$

where \(R_m = (T_a/T_b)^{1/2} = \text{Knudsen's constant}\)
\[ X = P_a d \] where \( P_a \) is the pressure above the sample and \( d \) is the internal diameter (in mm) of the sample tube, \( \alpha_{\text{He}} \) and \( \beta_{\text{He}} \) are experimental constants and \( \varnothing \) is a factor specific to the gas under consideration, defined as equal to 1 for helium and \( R_g \) is the thermal transpiration factor.

Bennett and Tompkins (1957) used the Liang equation to determine \( \varnothing \) at low pressure for CO, Ar, N\(_2\) and Kr which were 3.31, 2.70, 3.53 and 3.9, respectively. Rosenberg and Martel (1956) measured the variation of \( R_m \) at low pressures for Kr, determining a value of 3.84 for \( \varnothing \) for Kr. House and Jaycock (1975) redetermined the constants in the Liang equation which corresponded to the work by Bennett and Tompkins but the \( \varnothing \) value for Kr was found to be 3.7. Table 3.8 shows the \( \varnothing \) values used in this work.

Failure to correct for thermal transpiration at the lowest pressures would result in an error of almost 100% in the value of the pressure below the sharp thermal junction.

A thermal junction was present at the capacitance manometer measurement port. The heads were maintained at 322.15 ± 0.14K yielding a Knudsen constant, \( R_m \) of 0.962. This problem could have been overcome by using the heads without their integral heaters and relying on the thermostatted cabinet. This would have meant recalibrating the heads and also accepting a loss in accuracy i.e. approximately 0.5%, associated with running the heads at a lower temperature.
The maximum thermal transpiration error as expressed by the Knudsen equation is 4%. The problem of making a correction is difficult because the thermal junction is along the metal exit port. The parameters that have been determined for the Liang equation with a glass junction are not applicable. The metal junction is expected to be more diffuse and could possibly lead to a larger pressure differential (Los and Fergusson, 1952).

### Table 3.8. Experimental Constants for Specific Gases Used in the Liang Equation

<table>
<thead>
<tr>
<th>GAS</th>
<th>$\phi_g$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>2.70</td>
<td>Bennett and Tompkins (1957)</td>
</tr>
<tr>
<td>CO</td>
<td>3.31</td>
<td>&quot;</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.28</td>
<td>&quot;</td>
</tr>
<tr>
<td>Kr</td>
<td>3.70</td>
<td>House and Jaycock (1975)</td>
</tr>
</tbody>
</table>

#### 3.8. Adsorption Isotherm

##### 3.8.1. Measurement

The experimental procedure will be described with reference to Fig. 3.13 have the same plan but as both the low and high pressure sections the description is also applicable to the high pressure section.

The pressure is measured by two capacitance manometers, labelled P1 and P2 in Fig. 3.13. Gas leaked from the dosage region and admitted to the sample region via tap $T_1$. The gas is allowed to equilibrate.
parts and adsorbing onto the sample. The change detected by \( P_1 \) determines the amount of gas entering the sample region and the equilibrium pressure above the sample is measured by \( P_2 \). The use of two pressure gauges (rather than one) results in significantly improved accuracy by eliminating cumulative errors. This procedure is repeated, usually until the supply of gas in the dosage region is exhausted, to produce successive points on an isotherm. The dose volume may be increased by the additional use of the calibrated volume at the start of measuring. 8 to 20 points were measured per run and these points from different experimental runs were interspersed in order to represent the experimental scatter.

3.8.2. Calculation

3.8.2.1. Calculation of Equilibrium Pressure, \( P_e \)

The initial pressure reading \( (P_i) \) above the sample was noted before adsorption measurements were made. During the adsorption measurements, the equilibrium pressure \( (P_e) \) were recorded. Hence, the corrected equilibrium pressure \( (P_{ce}) \) was:

\[
P_{ce} = P_e - P_i
\]  

\( P_{ce} \) was the pressure above the thermal junction. To calculate the actual pressure below the thermal junction, the Liang equation, as previously described (Section 3.7) was used. The constants used are listed below:

\[
\begin{align*}
\alpha_{He/mmHg^{-2}mm^{-2}} & = 2.85 \\
\alpha_{He/N^{-2}m^2} & = 160.3 \\
\beta_{He/mmHg^{-1}mm^{-1}} & = 7.88 (1 - R_m) \\
\beta_{He/N^{-1}m} & = 59.1 (1 - R_m)
\end{align*}
\]

Therefore, the actual pressure above the sample, \( P \), may be obtained from:
where $R_g$ is the thermal transpiration factor derived from Liang's equation.

3.8.2.2. Calculation of the "Volume" Adsorbed

From the calibration results, the volume $V_1$, below the thermal junction may be calculated by the following equation:

$$V_1 = \frac{(V_s^c - V_s^w)}{(T_2 - T_1)} T_1$$

(3.9)

where $T_1$ is the temperature of the liquid $N_2/O_2$ bath and $T_2$ is at room temperature. The volume above the thermal junction, $V_2$, may be calculated by the following expression:

$$V_2 = V_c^w - V_1$$

(3.10)

The dosage volume, $V_3$ can be either:

$$V_3 = V_d$$

or

$$V_3 = V_d + V_c$$

(3.11)

The total volume of gas present in the sample region, $V_{dos}$ at STP is given by:

$$V_{dos} = \frac{P_1 \times V_3 \times 273.15}{760 \times T_2}$$

(3.12)
where $P_l$ is the pressure in mmHg in the dosage region. The volume of gas present above the thermal junction ($V_{T_2}$) is given by:

$$V_{T_2} = \frac{P_{ce} \times V_2 \times 273.15}{760 \times T_2}$$

The volume of gas present below the thermal junction, $V_{T_1}$ at STP is given by:

$$V_{T_1} = \frac{P \times V_1 \times 273.15}{760 \times T_1}$$

Hence, the volume of gas adsorbed per gram of sample is:

$$V = \frac{(V_{dos} - V_{T_2} - V_{T_1})}{W}$$

where $W$ is the weight of sample in grammes. The volume of gas adsorbed at STP ($V$) may be converted to $V_a$, the number of moles adsorbed by the following expression:

$$V_a = \frac{V}{22414}$$

The isotherms presented in this work are represented as $V_a$ (mmol g$^{-1}$) versus relative pressure ($P/P_0$) where $P_0$ is the saturation vapour pressure of the adsorbate.

The calculation of the adsorption isotherm given above is based on the ideal-gas law. The range of pressures and temperatures used in this investigation do not significantly deviate from ideality. Thus no corrections were made for the non-ideality of the pressure used in the above calculation.

The data presented in this work was not corrected for the tap volume changes.
CHAPTER 4

RESULTS AND DISCUSSION
Due to the size of this chapter, the results and discussion presented are sectioned into the following themes:

1. Barium sulphate with various amounts of STPP.
2. Normalization procedure for submonolayer data.
3. Carbon monoxide as a gas probe.
4. CAEDMON method.
5. Adsorption of different adsorbates onto barium sulphate.
6. Comparison of two samples of barium sulphate.
7. The effect of adsorption temperatures.

4.1. Barium sulphate with various amounts of sodium tripolyphosphate (STPP)

The objective of this work was to determine the usefulness and sensitivity of heterogeneity analysis (the HILDA method) in the study of the chemically modified surfaces of barium sulphate. The surfaces were chemically modified by the pre-adsorption of various amounts of STPP. Nitrogen and carbon monoxide gases were used to probe the surfaces of these barium sulphate at 77.8K. This section deals with the nitrogen data which are used to estimate the specific surface area, and are analysed by the HILDA method. Within the latter method, the smoothing procedure followed throughout this work is discussed, and the Hill-de Boer and Langmuir models are compared for the same data.

Three samples were studied:

i) Sample 1: precipitated barium sulphate

ii) Sample 2: barium sulphate with 38% monolayer coverage of STPP

iii) Sample 3: barium sulphate with a monolayer coverage of STPP

The preparation and physical characterization of these samples are given in Chapter 3.
4.1.1. Isotherms of nitrogen

The isotherms determined at 77.8K are shown in Figs. 4.1a, 4.1b and 4.1c. All three isotherms show an initial steep gradient to the knee region, then a small linear region followed by a very steep rise when approaching the saturation vapour pressure of nitrogen. The isotherms are of "type II" in accordance with the Brunauer, Deming, Deming and Teller (1940) classification.

These isotherms show a decrease in the amount of nitrogen adsorbed as the STPP coverage increases and this reduction is best observed below a relative pressure of 0.01, see Figs. 4.1a and 4.1b. The effect of monolayer coverage of STPP (or less) diminishes above a relative pressure of 0.01 and becomes difficult to distinguish as the relative pressure approaches 1.

In the higher pressure region i.e. above a relative pressure of 0.15, the isotherm for sample 2 shows much increased experimental scatter. Possible causes for this include fluctuation of the temperature of the liquid N$_2$/O$_2$ bath due to variations in the level of the liquid N$_2$/O$_2$ mixture or that a temperature gradient was set up in the bath due to the stirrer stopping. Another factor which could cause this scatter would be due to not measuring the equilibrium pressure over a longer period of time. These factors were, however, examined in detail and were eliminated as the cause of the experimental scatter. All the points on the isotherm for sample 2 have been included in the BET plot and the Heterogeneity Analysis.
Fig. 4.1a Adsorption isotherms of nitrogen at 77.8K

Sample 1

Sample 2

Sample 3

Amount adsorbed (mmol g⁻¹)

Relative pressure
Fig. 4.1b Adsorption isotherms of nitrogen at 77.8K

Sample 1

Sample 2

Sample 3

Amount adsorbed (mmol g⁻¹)

Relative pressure
Fig. 4.1c Adsorption isotherms of nitrogen at 77.8K

Sample 1

Sample 2

Sample 3

Amount adsorbed (mmol g⁻¹)

Relative pressure
4.1.2. Estimation of the specific surface areas

These isotherms were used to estimate the surface areas of the three samples by the Brunauer, Emmett and Teller (BET) (1938) method.

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>TEMPERATURE /K</th>
<th>SATURATION VAPOUR /mmHg</th>
<th>RELATIVE PRESSURE RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>77.8</td>
<td>801.42</td>
<td>1.25x10⁻⁸ - 1.00</td>
</tr>
<tr>
<td>N₂</td>
<td>80.8</td>
<td>1120.69</td>
<td>8.95x10⁻⁹ - 0.89</td>
</tr>
<tr>
<td>N₂</td>
<td>81.6</td>
<td>1220.08</td>
<td>8.20x10⁻⁹ - 0.82</td>
</tr>
<tr>
<td>Kr</td>
<td>77.8</td>
<td>1.76</td>
<td>3.64x10⁻⁶ - 0.70</td>
</tr>
<tr>
<td>Ar</td>
<td>77.8</td>
<td>219.48</td>
<td>4.56x10⁻⁸ - 1.00</td>
</tr>
<tr>
<td>CO</td>
<td>77.8</td>
<td>526.34</td>
<td>1.90x10⁻⁸ - 0.0015</td>
</tr>
</tbody>
</table>

The saturation vapour pressures of the adsorbates used in this study were obtained from the following workers:— Jacobsen (1975) for nitrogen, Weast (1984) for argon and carbon monoxide and Meihui and Crommelin (1937) for krypton.

To obtain the monolayer amount, \( V_m \), and the BET 'C' constant, plots of \( P/V_{ads} (P_o - P) \) vs \( P/P_o \) were made, (see Fig 4.2). Table 4.2 shows the parameters used, and the calculated specific surface area. A linear regression routine was used to fit the BET data and the analysis is given in Table 4.3, with the specific surface areas.

The results show that the specific surface area of barium sulphate decreases with increasing coverage of STPP. A reduction of 4.7% and 32.2% is found in the specific surface areas of 38% monolayer coverage and 100% monolayer coverage of STPP on the surfaces of barium sulphate, respectively.
Fig. 4.2 Nitrogen BET plot

- Sample 2
- Sample 3
<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>Temperature /K</th>
<th>Relative pressure range</th>
<th>BET 'C' constant</th>
<th>$E_1$ /kJmol$^{-1}$</th>
<th>$\sigma_m$ nm$^2$ molec$^{-1}$</th>
<th>$V_m$ mmolg$^{-1}$</th>
<th>S m$^2$g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N$_2$</td>
<td>77.8</td>
<td>0.05-0.35</td>
<td>58.5</td>
<td>8.20</td>
<td>0.162</td>
<td>0.0887</td>
<td>8.65</td>
</tr>
<tr>
<td>2</td>
<td>N$_2$</td>
<td>77.8</td>
<td>0.04-0.31</td>
<td>26.2</td>
<td>7.70</td>
<td>0.162</td>
<td>0.0845</td>
<td>8.24</td>
</tr>
<tr>
<td>3</td>
<td>N$_2$</td>
<td>77.8</td>
<td>0.03-0.38</td>
<td>60.1</td>
<td>8.20</td>
<td>0.162</td>
<td>0.0600</td>
<td>5.86</td>
</tr>
<tr>
<td>1</td>
<td>Kr</td>
<td>77.8</td>
<td>0.05-0.25</td>
<td>102.0</td>
<td>12.4</td>
<td>0.195</td>
<td>0.0465</td>
<td>5.45</td>
</tr>
<tr>
<td>2</td>
<td>Kr</td>
<td>77.8</td>
<td>0.04-0.28</td>
<td>38.5</td>
<td>11.8</td>
<td>0.195</td>
<td>0.0438</td>
<td>5.27</td>
</tr>
<tr>
<td>3</td>
<td>Kr</td>
<td>77.8</td>
<td>0.04-0.28</td>
<td>31.0</td>
<td>11.6</td>
<td>0.195</td>
<td>0.0422</td>
<td>5.09</td>
</tr>
<tr>
<td>Sample</td>
<td>Gas</td>
<td>Temperature /K</td>
<td>Correlation Coefficient</td>
<td>r.m.s.</td>
<td>Intercept</td>
<td>Slope</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-----</td>
<td>----------------</td>
<td>-------------------------</td>
<td>--------</td>
<td>-----------</td>
<td>-------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>N2</td>
<td>77.8</td>
<td>0.9994</td>
<td>0.0025</td>
<td>0.0086</td>
<td>0.494</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>N2</td>
<td>77.8</td>
<td>0.9824</td>
<td>0.0085</td>
<td>0.0201</td>
<td>0.507</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>N2</td>
<td>77.8</td>
<td>0.9987</td>
<td>0.0042</td>
<td>0.0123</td>
<td>0.730</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Kr</td>
<td>77.8</td>
<td>0.9998</td>
<td>0.0009</td>
<td>0.0094</td>
<td>0.951</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Kr</td>
<td>77.8</td>
<td>0.9999</td>
<td>0.0007</td>
<td>0.0264</td>
<td>0.991</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Kr</td>
<td>77.8</td>
<td>0.9986</td>
<td>0.0040</td>
<td>0.0342</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Krypton gas was also used to estimate the specific surface areas of samples 1, 2 and 3. The isotherms of krypton on sample 1, 2 and 3 are shown in Fig. 4.3. The experimental points for the Kr-BET analysis were determined between a relative pressure range of 0.05 to 0.3. The Kr-BET plots are shown in Fig. 4.4. The Kr-BET plots are linear and show better linearity than the N₂-BET plots. The parameters used are given in Table 4.2 above. These results also show that the specific surface area of sample 1 decreases with increasing coverage of STPP. With krypton, a reduction of 5.6% and 9.0% is found in the specific surface areas of 38% monolayer coverage and 100% monolayer coverage of STPP on the surfaces of samples 1, respectively.

The change in the specific surface area between samples 1 and 2 is similar from N₂ and Kr, however the change from sample 1 to sample 3 from N₂ is seen to be much larger than for Kr, see Fig 4.4a. This would suggest that the nitrogen molecule may be more sensitive than krypton for these preadsorbed samples. The N₂ results show a larger surface area compared to the Kr results for the same adsorbents. This has also been found in other investigations (Sing and Swallow (1965), Bergman and Paterson (1961)).

The BET 'C' constants for Kr decrease with increasing STPP while those for N₂ are very similar at 0 and 100% coverage, with a lower value is given for the 38% case where we see maximum scatter.

The trend of the E₁ values is the same, however the magnitudes are similar for all three samples for both Kr and N₂.
Fig. 4.3 Adsorption isotherms of krypton at 77.8K

- Sample 1
- Sample 2
- Sample 3

Relative pressure vs. Amount adsorbed (cm$^3$ g$^{-1}$)
Fig. 4.4 BET plots of krypton at 77.3K

Sample 1

* Sample 2

△ Sample 3
Fig. 4.4a  Specific surface area at barium sulphate with various amounts of preadsorbed STPP

- Nitrogen
- Krypton

Specific surface area (m² g⁻¹)

STPP coverage (% monolayer)
4.1.2.1. Comparison of BET isotherm with experimental isotherm

In the absence of low pressure data, the BET equation is sometimes extrapolated to estimate the low pressure isotherm given the constants from the BET region. Given the detailed data here, it is interesting to test this approximation for the systems under investigation.

Thus, the BET parameters i.e. \( V_m \) and BET 'C' constant were used to generate the respective isotherms for \( N_2 \) and Kr on barium sulphate outside the BET range. These are shown in Figs. 4.5a-b, and Figs. 4.6a-b for \( N_2 \) and Kr respectively represented by the smooth line, while the points represent the original raw data. The generated isotherm fitted the BET pressure range (i.e. \( P/P_0 : 0.05 \) to 0.35) only. The generated \( N_2 \) BET isotherm shows a much lower adsorption below 50 mmHg and greater adsorption above 350 mmHg, whereas, the Kr BET isotherm shows a lower adsorption below 0.08 and higher adsorption above 0.5 mmHg.

4.1.3. Heterogeneity Analysis

4.1.3.1. Smoothing procedure

The isotherms for the three samples were used to calculate the SED using the MILDA method, discussed in chapter 2. The parameter used in MILDA are given in Tables 2.1 and 2.2. The smoothing procedure used on this work was:

i) the experimental data was plotted on graph paper and then a smoothed curve was drawn by hand when required.

ii) then this smoothed curve was further smoothed using Dataset program (see chapter 2).
Fig. 4.5a BET fit to the adsorption isotherm of nitrogen on sample 1 at 77.8K

Equilibrium pressure (mmHg)

Amount adsorbed (cm$^3$ g$^{-1}$)
BET fit to the adsorption isotherm of nitrogen on sample 1 at 77.8K
Fig. 4.6a BET fit to the adsorption isotherm of krypton on sample 1 at 77.8K
Fig. 4.6b BET fit to the adsorption isotherm of krypton on sample 1 at 77.8K
Great care was taken to check that the smoothed curve represented a satisfactory best fit to the experimental data and a routine called MULTIPLOT was utilised. This routine plots the experimental data with the fitted curve for the whole pressure range studied. Then any part of the fitted data may be examined within a small pressure range.

The parameters obtained from the heterogeneity analysis are presented in Tables 4.4, 4.5 and 4.6. A number of points emerge from these parameters. The smoothing factor SM1 is similar for the 3 samples reflecting similar accuracy of the raw data. However, for SM2, describing the ease of fit to the SED, the Hill-de Boer gives much smaller values compared to the Langmuir values, which suggests that the fits are better for the former model.

For the nitrogen data using the Hill-de Boer model, the quality of fit, reflected in the r.m.s. values, are much better than those obtained using the Langmuir model. This also applies to the CO data for sample 2. The r.m.s. values for sample 2 are higher compared to sample 1, and sample 1 r.m.s. values are higher than sample 3 for both models. This would indicate that the scatter of experimental data is greater in sample 2 followed by sample 1 and the least scatter found in sample 3. The results of the fitted curve are shown in Appendix 1.

4.1.3.2. Hill-de Boer model

The Hill-de Boer isotherm was used to determine the SED's for sample 1, 2 and 3. (Fig. 4.7a). These SED's suggest that multilayer formation occurs at approximately 5 kJmol$^{-1}$ before the steep rise in
<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>NUMBER OF DATA POINTS</th>
<th>MODEL</th>
<th>MULTILAYER CORRECTION</th>
<th>NUMBER OF ITERATIONS</th>
<th>r.m.s.</th>
<th>SM1</th>
<th>SM2</th>
<th>Vm/mmolg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>153</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0137</td>
<td>0.0011</td>
<td>0.0168</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>153</td>
<td>HdB</td>
<td>NO</td>
<td>44</td>
<td>0.0107</td>
<td>0.0011</td>
<td>0.0055</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>144</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0091</td>
<td>0.0012</td>
<td>0.0094</td>
<td>0.0861</td>
</tr>
<tr>
<td>N₂</td>
<td>153</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3256</td>
<td>0.0011</td>
<td>0.1426</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>144</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.3019</td>
<td>0.0012</td>
<td>0.1445</td>
<td>0.0861</td>
</tr>
<tr>
<td>N₂</td>
<td>153 (RANDOMISED)</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0112</td>
<td>0.0012</td>
<td>0.0115</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>153 (RANDOMISED)</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3037</td>
<td>0.0012</td>
<td>0.2249</td>
<td>0.2164</td>
</tr>
</tbody>
</table>
TABLE 4.5  The results of the HILDA analysis for barium sulphate 1 preadsorbed with 38% monolayer coverage of sodium triphosphate at 77.8K

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>NUMBER OF DATA POINTS</th>
<th>MODEL</th>
<th>MULTILAYER CORRECTION</th>
<th>NUMBER OF ITERATIONS</th>
<th>r.m.s.</th>
<th>SM1</th>
<th>SM2</th>
<th>Vm/mmolg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>133</td>
<td>HdB</td>
<td>NO</td>
<td>13</td>
<td>0.0192</td>
<td>0.0012</td>
<td>0.0027</td>
<td>0.2169</td>
</tr>
<tr>
<td>N₂</td>
<td>108</td>
<td>HdB</td>
<td>YES</td>
<td>13</td>
<td>0.0089</td>
<td>0.0013</td>
<td>0.0011</td>
<td>0.0798</td>
</tr>
<tr>
<td>N₂</td>
<td>133</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3985</td>
<td>0.0012</td>
<td>0.4994</td>
<td>0.2169</td>
</tr>
<tr>
<td>N₂</td>
<td>108</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.3353</td>
<td>0.0013</td>
<td>0.4332</td>
<td>0.0798</td>
</tr>
<tr>
<td>CO</td>
<td>80</td>
<td>HdB</td>
<td>NO</td>
<td>12</td>
<td>0.0786</td>
<td>0.0017</td>
<td>0.0083</td>
<td>0.0302</td>
</tr>
<tr>
<td>CO</td>
<td>80</td>
<td>HdB</td>
<td>NO</td>
<td>66</td>
<td>0.0687</td>
<td>0.0017</td>
<td>0.0</td>
<td>0.0302</td>
</tr>
<tr>
<td>CO</td>
<td>80</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.9678</td>
<td>0.0017</td>
<td>0.3807</td>
<td>0.0302</td>
</tr>
</tbody>
</table>
TABLE 4.6  

The results of the HILDA analysis for barium sulphate 1 preadsorbed with 100% monolayer coverage of sodium triphosphate at 77.8K

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>NUMBER OF DATA POINTS</th>
<th>MODEL</th>
<th>MULTILAYER CORRECTION</th>
<th>NUMBER OF ITERATIONS</th>
<th>r.m.s.</th>
<th>SM1</th>
<th>SM2</th>
<th>Vm/ mmolg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>99</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0123</td>
<td>0.0016</td>
<td>0.0045</td>
<td>0.1742</td>
</tr>
<tr>
<td>N₂</td>
<td>89</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0044</td>
<td>0.0015</td>
<td>0.0021</td>
<td>0.0579</td>
</tr>
<tr>
<td>N₂</td>
<td>99</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.2040</td>
<td>0.0016</td>
<td>0.0436</td>
<td>0.1742</td>
</tr>
<tr>
<td>N₂</td>
<td>89</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.1545</td>
<td>0.0015</td>
<td>0.0409</td>
<td>0.0579</td>
</tr>
</tbody>
</table>
Fig. 4.7a The site energy distribution functions obtained by HILDA from the Hill–de Boer analysis of the adsorption of nitrogen at 77.8K.
the energy distribution. However, a fuller examination of the energy distribution (Fig. 4.7b) shows that some features are present before the steep rise.

The SED’s obtained from the multilayer corrected nitrogen data are shown in Fig. 4.7c. The multilayer correction is used to provide a consistent method of termination of the energy distribution. Both the multilayer corrected and uncorrected SED’s show identical features labelled A to D with the subscript denoting the sample number. An extra feature labelled E is present for the multilayer corrected SED’s. Peak E indicates consistency with Fig. 4.7b which shows changes of slope before the real multilayer rise.

The results show that as the coverage of STPP increases, the effect on the areas under the SED in the different regions is as follows: A shows a clear decrease, C increases while B, D and E do not show monotonic behaviour.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Region A</th>
<th>Region B</th>
<th>Region C</th>
<th>Region D</th>
<th>Region E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.16</td>
<td>22.80</td>
<td>9.67</td>
<td>31.57</td>
<td>14.80</td>
</tr>
<tr>
<td>2</td>
<td>9.33</td>
<td>14.92</td>
<td>11.83</td>
<td>32.85</td>
<td>31.07</td>
</tr>
<tr>
<td>3</td>
<td>4.87</td>
<td>18.33</td>
<td>32.62</td>
<td>42.57</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Table 4.7 shows the area of the SED for each region for Fig. 4.7c. Region A decreases by 55.9% for 38% STPP coverage and by 77.0% for monolayer coverage. Region C increases by 22.3% for 38% STPP coverage and 273% for monolayer coverage and since, no general trend
Fig. 4.7b Detailed plot of the site energy distribution in Fig. 4.7a

Sample 1  -- -- -- -- Sample 2  -- -- -- Sample 3
Fig. 4.7c The site energy distribution of Fig. 4.7a with the application of the multilayer correction

Sample 1
Sample 2
Sample 3

\( U \) (kJmol\(^{-1}\))
is observed for regions B, D and E, the areas of region A and B were compared with the areas of region C, D and E. The results are presented below.

**TABLE 4.8. Comparison of areas of regions A and B with regions C, D and E**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area (%)</th>
<th>Difference from Sample 1</th>
<th>Region C+D+E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.96</td>
<td>-</td>
<td>56.04</td>
</tr>
<tr>
<td>2</td>
<td>24.25</td>
<td>19.71</td>
<td>75.75</td>
</tr>
<tr>
<td>3</td>
<td>23.20</td>
<td>20.76</td>
<td>76.80</td>
</tr>
</tbody>
</table>

This table 4.8. shows that majority of high energy sites (mainly represented by region A) are lost by adsorbing 38% STPP, further coverage up to monolayer STPP shows very little difference. The low energy sites increase dramatically by adsorbing 38% STPP but further coverage of monolayer STPP shows very little difference.

4.1.3.3. **Langmuir model**

The Langmuir model was applied to the same isotherms and Fig. 4.8a shows the full SED's. In this case there appears to be a very clear indication of formation multilayer close to 8.65 kJmol⁻¹. To study the features above 10 kJmol⁻¹, Fig. 4.8b was plotted on a more appropriate scale. The energy distribution shows individual peaks or regions (i.e. U towards 0) within the SED and not only at the ends. This is not generally found for the Hill-de Boer or Fowler-Guggenheim model SED's.
Fig. 4.8a The site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of nitrogen at 77.8K.

Sample 1

Sample 2

Sample 3

$F(U)$ (mole$^{-1}$)

$U$ (kJ mol$^{-1}$)
Fig. 4.8b  Detailed plot of the site energy distributions from Fig. 4.8a

Sample 1  ---  Sample 2  ---  Sample 3

$F(U)$ (mole$^{-1}$)

$U$ (kJ$\text{mol}^{-1}$)
The Langmuir SED appears elongated and stretched in the "vertical" direction with respect to the Hill-de Boer result, however the general features of number of peaks, positions and relative heights are very similar for these two models of adsorption onto uniform surfaces.

The SED's obtained from the multilayer corrected data is represented in Fig. 4.8c. This shows that new features are present between 8 and 11 kJmol\(^{-1}\), labelled F and G but features A to E are identical to those in Fig. 4.8b. Examination of the full range SED's in Fig. 4.8a shows no feature between 8.65 and 10.8 kJmol\(^{-1}\) which is not consistent. The peak area for Fig. 4.8c. is given in Table 4.9.

From the SED's and the table 4.9 show that the area of region A decreases with increasing coverage of STPP, and the area of region E increases with increasing coverage of STPP on the surface of barium sulphate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.94</td>
<td></td>
<td>9.53</td>
<td>12.84</td>
<td>2.00</td>
<td>42.80</td>
<td>11.89</td>
</tr>
<tr>
<td>2</td>
<td>8.74</td>
<td>2.26</td>
<td>4.54</td>
<td>3.54</td>
<td>13.81</td>
<td>18.97</td>
<td>48.12</td>
</tr>
<tr>
<td>3</td>
<td>3.52</td>
<td>5.73</td>
<td>5.84</td>
<td>5.55</td>
<td>25.89</td>
<td>53.47</td>
<td></td>
</tr>
</tbody>
</table>

Region B for sample 1 is very difficult to distinguish since it overlaps with region C, but for samples 2 and 3 region B is easily distinguished. The SED suggests that region B has translated from approximately 14.8 kJmol\(^{-1}\) from the bare surface of barium sulphate.
Fig. 4.8c The site energy distribution of Fig. 4.8a with the application of the multilayer correction

![Energy Distribution Graph]

- Sample 1
- Sample 2
- Sample 3
to approximately 16 kJmol⁻¹ for a complete monolayer coverage of STPP. Again, the individual regions were grouped so that the areas would give information about high and low energy sites. The combined areas of region A to D were compared to the combined areas of region E to G, see table below.

```
<table>
<thead>
<tr>
<th>Sample</th>
<th>Region A,D Area %</th>
<th>difference from Sample 1</th>
<th>Region E to G Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.31</td>
<td>-</td>
<td>56.69</td>
</tr>
<tr>
<td>2</td>
<td>19.08</td>
<td>24.23</td>
<td>80.92</td>
</tr>
<tr>
<td>3</td>
<td>20.64</td>
<td>22.67</td>
<td>79.36</td>
</tr>
</tbody>
</table>
```

This table 4.10 shows that the high energy sites are lost with 38% STPP coverage and very little difference in area is found for the monolayer coverage of STPP. The low energy sites increase substantially with 38% STPP coverage but virtually no change is observed for the monolayer coverage of STPP.

The Hill-de Boer and Langmuir model give very similar information from the energy distribution for the interaction of N₂ on samples 1, 2 and 3. Both models show that high energy sites decrease dramatically with 38% STPP coverage but only a small difference is observed between these 38% STPP and monolayer coverage samples.
4.2. Modified Normalization Procedure For Submonolayer Data

Adsorption data that is well below the monolayer for various adsorbents are difficult to compare using the Heterogeneity analysis, as the energy distributions are normalized to unity at the maximum pressure measured rather than at the monolayer value. However, in the special case where adsorption isotherms have the same surface area or monolayer capacity but differing adsorption properties at low pressures, we suggest a modified normalisation procedure in order to compare submonolayer SED's. Consider Fig. 4.9. The HILDA method normalizes all three isotherms at $P_N$ and $V_N$ given full ranging data, and thus the three energy distributions obtained would correctly reflect the differences at the lower pressures. However if data was limited to a pressure well below the monolayer for the three samples, eg $P_{sub}$, then HILDA would normalize all three isotherms at $P_{sub}$ so that $a_1$, $b_2$, and $c_3$ would all go to the same value of 1. We may then compare relative features with such energy distributions, eg the ratio of peak heights within each distribution, but not a single peak height in the different distributions or the overall area.

To restore the differences $a_1$, $b_2$ and $c_3$ for this ideal case of termination at the same monolayer value, we modify the HILDA routine to "un-normalise" at $P_{sub}$. This is an approximation method for samples with similar surfaces. We have used this procedure to compare appropriate low pressure data and have tested the approximation where we have the full range of data.
4.2.1. Comparison of the normalized and the full range SED's

4.2.1.1. Hill-de Boer model

Using the above normalizing procedure discussed above, the SED's from the HILDA method for the Hill-de Boer model are shown in Fig. 4.10. These SED's were compared with the SED's for the full range isotherm data of N₂ for sample 1, 2 and 3 shown in Fig. 4.11, but these SED's are terminated at 8.0 kJmol⁻¹ (which is equivalent to 1 mmHg on the pressure scale) for ease of comparison. The SED's for the two procedures are virtually identical and they show a reduction in sites above 11.5 kJmol with increasing coverage of STPP on the surface of barium sulphate.

### TABLE 4.11. Peak areas determined from the site energy distributions in Fig 4.10

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.00</td>
<td>15.37</td>
<td>12.40</td>
<td>15.52</td>
<td>10.68</td>
<td>13.03</td>
</tr>
<tr>
<td>2</td>
<td>23.06</td>
<td>12.17</td>
<td>13.20</td>
<td>20.25</td>
<td>13.64</td>
<td>17.68</td>
</tr>
<tr>
<td>3</td>
<td>11.47</td>
<td>3.70</td>
<td>18.12</td>
<td>24.51</td>
<td>19.46</td>
<td>22.74</td>
</tr>
</tbody>
</table>
Fig. 4.10 The site energy distribution of Fig. 4.7a analysed up to 1.0 mmHg (normalized)

Sample 1
Sample 2
Sample 3

\[ F(U) \text{ (mol.kJ)}^{-1} \]

\[ U \text{ (kJ.mol}^{-1}) \]

Points of interest:
- \( A_1 \)
- \( B_1 \)
- \( C_1 \)
- \( D_1 \)
- \( E_1 \)
- \( F_1 \)
- \( A_2 \)
- \( B_2 \)
- \( C_2 \)
- \( D_2 \)
- \( E_2 \)
- \( F_2 \)
- \( A_3 \)
- \( B_3 \)
- \( C_3 \)
- \( D_3 \)
- \( E_3 \)
- \( F_3 \)
Fig. 4.11 The site energy distributions of Fig. 4.7a above 8kJmol\(^{-1}\) (equivalent to 1mmHg)
The major difference between the full range SED's (Fig 4.11) and the normalized SED's (Fig 4.10) is that the former are more smoothed. This is because 80 points were used for the Dataset smoothing routine for the full complement of data. Thus, for the normalized Eds (1 mmHg) 80 points were used, but for the full range SED's less than 80 points were used. Due to this smoothing peak B is clearly observed in Fig. 4.10 for samples 2 and 3 but not in Fig. 4.11.

Table 4.11 shows the area under the individual regions for Fig. 4.10. The area under regions A and B decrease with increasing STPP coverage on the surface of barium sulphate.

The above procedure was repeated for the Langmuir model to establish the differences between the two models. Fig. 4.12 shows the normalized SED's and Fig. 4.13 shows the full range SED's but terminated at 12.0 kJmol$^{-1}$. Both Fig. 4.12 and Fig. 4.13 show that they are similar. The key feature within the SED's show that above 16.0 kJmol$^{-1}$ (region A) decrease with increasing coverage of STPP on the surface of barium sulphate. The full range SED's is much smoother than the normalized SED due to the smoothing procedure used, discussed earlier. Hence, for the normalized SED's two peaks are found for region A for samples 1 and 2, but in the full range SED's suggests that two peaks are combined into one. Region B is shown clearly in the normalized SED's for sample 1. Which indicates that region B is translated from 14.8 kJmol$^{-1}$ to approx 16.0 kJmol$^{-1}$ with increase in the STPP coverage on the surface of barium sulphate.
Fig. 4.12 The site energy distributions of Fig. 4.8a analysed upto 1.0mmHg (normalized)
Fig. 4.13 The site energy distributions of Fig. 4.8a above 12.0 kJ mol$^{-1}$ (equivalent to 1 mm Hg)
Table 4.12 shows the area under the individual regions for Fig. 4.12. The major feature, region A decreases with increasing coverage of STPP.

Both the Hill-de Boer and Langmuir models show very similar information within the SED's for the interaction of nitrogen with the surfaces of sample 1, 2 and 3. However, only the Langmuir model indicate the translation of peak E within the energy range of 14.6 kJmol\(^{-1}\) and 16.7 kJmol\(^{-1}\).

**TABLE 4.12  Peak areas determined from the site energy distributions in Fig 4.12**

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Area Region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>35.70</td>
</tr>
<tr>
<td>2</td>
<td>15.54</td>
</tr>
<tr>
<td>3</td>
<td>11.60</td>
</tr>
</tbody>
</table>

This normalization procedure show reasonable agreement in this case as small changes in the BET area are found for sample 1, 2 and 3. If the \(V_m\) values for these samples were the same, then identical results from both methods would be obtained.
4.3. **Carbon monoxide as probe molecule**

Carbon monoxide was used to probe the surface of barium sulphate with various amounts of STPP. This was done to see the effect of the strong dipole moment interaction with the adsorbent surface, and furthermore, to compare the heterogeneity analysis results with that of nitrogen, which has a quadrupole moment.

4.3.1. **Isotherms**

CO was used to probe the surfaces of sample 1 and 2. The pressure range for this study was from $10^{-5}$ to 1 mmHg, which are shown in Fig 4.14a and 4.14b. Both isotherms show a very steep rise at very low pressure, which is steeper than for $N_2$, followed by a sharp knee region to one of much lower slope at high pressures. Sample 1 adsorbs CO more strongly than sample 2 throughout the pressure range studied, due to the change in electric field by the presence of STPP.

Comparing the isotherms of CO and $N_2$ (Figs 4.19a, 4.19b and 4.19c) shows that CO is much strongly adsorbed than $N_2$ for sample 1 below a pressure of 1 mmHg, due to the strong dipole moment.

The smoothing parameters for the CO data on sample 1 and 2 are given on Tables 4.4 and 4.5. The tables show that the r.m.s. is small for the Hill-de Boer model than the Langmuir model, and also SM2 is larger for the Langmuir model.
Fig. 4.14a Adsorption isotherms of carbon monoxide at 77.8K

Sample 1

Sample 2
Fig. 4.14b Adsorption isotherms of carbon monoxide at 77.8K

Sample 1

Sample 2

Amount adsorbed (mmol/g)

Relative pressure
4.3.2. Heterogeneity Analysis

4.3.2.1. Hill-de Boer model

The CO data was well below the monolayer region, hence the normalization procedure was employed to obtain a better comparison of the surfaces of sample 1 and 2. The SED's are shown in Fig. 4.15, which were obtained from the HILDA method using the Hill-de Boer model.

The dominant feature in the SED's is above 12 kJmol\(^{-1}\) (labelled regions A and B) but below 12 kJmol\(^{-1}\) very little difference of information in the SED's may be observed. At high energy, sample 1 suggests that further higher energy sites (> 14.5 kJmol\(^{-1}\)) may be present. Hence further information may be found for the higher energy sites for CO compared with N\(_2\), if studied at much lower pressures (below 10\(^{-5}\) mmHg).

Two main peaks are shown above 12.0 kJmol\(^{-1}\) for both samples, however, region A decreases substantially with the presence of 38% monolayer coverage of STPP for sample 2. In region B, the peak height increases slightly.

The N\(_2\) SED's showed the lowering of all the high energy sites (features) whereas CO shows a dramatic lowering of one peak at 13.8 kJmol\(^{-1}\) but not the peak at 13.2 kJmol\(^{-1}\). This is a very remarkable result suggesting that CO adsorbs preferentially on to the barium sulphate surface at 13.8 kJmol\(^{-1}\) i.e. a specific site with respect to the remaining sites. The area under the regions are given in Table 4.13. This table shows that the area of region A decreases by 81.5% and region B increases by 35.9%. 
Fig. 4.15 The site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of carbon monoxide (normalized at 1 mmHg)

--- Sample 1 --- Sample 2

--- Sample 2 --- Sample 1

$F(U)$ (molec$^{-1}$) vs $U$ (kJmol$^{-1}$)

$U$ (kJmol$^{-1}$)

$F(U)$ (molec$^{-1}$)

$A_1$, $B_1$, $B_2$, $A_2$
4.3.2.2. Langmuir model

The Langmuir model was used to determine the SED's for the normalized CO data for sample 1 and 2, see Fig. 4.16. The dominant feature is found above 17.0 kJmol\(^{-1}\). This feature, labelled A on the SED, decreases substantially with 38% monolayer coverage of STPP on the surface of barium sulphate. Also, region A shifts slightly to lower energy for sample 2, which was also observed in the Hill-de Boer SED's.

The area under region A for both samples are shown in the table below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area of Region A %</th>
<th>Remaining area of SED %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>68.1</td>
<td>31.9</td>
</tr>
<tr>
<td>2</td>
<td>49.7</td>
<td>50.3</td>
</tr>
</tbody>
</table>

The area of region A was reduced by 18.4% for the 38% STPP monolayer coverage on the surface of barium sulphate.

The Hill-de Boer and Langmuir model SED's are very different. The Langmuir SED's show large discrete region compared to the Hill-de Boer SED's.

**TABLE 4.13** Peak areas of SED's in Fig 4.15

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.14</td>
<td>27.10</td>
<td>3.24</td>
<td>7.33</td>
<td>4.34</td>
<td>5.22</td>
<td>8.91</td>
<td>11.69</td>
</tr>
<tr>
<td>2</td>
<td>5.69</td>
<td>36.82</td>
<td>3.60</td>
<td>8.63</td>
<td>8.35</td>
<td>0.44</td>
<td>6.35</td>
<td>19.85</td>
</tr>
</tbody>
</table>
Fig. 4.16 The site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of carbon monoxide (normalized at 1mmHg)

Sample 1

Sample 2

$P(U)$ (mol kJ mol$^{-1}$)

$U$ (kJ mol$^{-1}$)
4.4. **CAEDMON Method**

The main focus of the work of this thesis has been to investigate surface changes and their detection by different gases, utilising a given analysis method, HILDA. We have, however, selected some data for analysis by the well-known CAEDMON method. CAEDMON, has been used to compare the chemically modified surfaces of barium sulphate with preadsorption of STPP. The method of termination of the data was also compared using the multilayer correction and the BET method.

The CAEDMON method was used to analyse the nitrogen data for samples 1, 2 and 3 at 77.8K. Table 4.14 shows the parameters from the analysis. Since this method requires the termination of the data at the monolayer volume, both the BET and the multilayer correction monolayer volumes were utilized. Table 4.14 shows that the r.m.s. for the BET termination are smaller compared to the multilayer concentration. Figs 4.17 and 4.18 shows the SED's at the BET and multilayer correction monolayer volume termination. The two termination methods give very similar SED's above 6 kJmol$^{-1}$, however below 6 kJmol$^{-1}$, differences are observed.

The CAEDMON method SED's are in the form of a histogram for the number of patches considered. In this work 20 patches were used and the results have been plotted as a continuous SED's on the same energy scale as the Hill-de Boer model (i.e. $- RT \ln K = 0$, $U \equiv 8.87$ kJmol$^{-1}$) by joining the midpoints of the bars on the histogram. For a comparison with the Langmuir model at $- RT \ln K = 0$, $U \equiv 11.42$ kJmol$^{-1}$ would be used to obtain the correct energy scales. The CAEDMON method and the Hill-de Boer model SED's from
Fig. 4.17 The site energy distribution functions obtained by CAEDMON for the nitrogen adsorption data on samples 1, 2 and 3 at 77.8K terminated at the BET monolayer volumes.
Fig. 4.18 The site energy distribution functions obtained by CAEDMON for the multilayer corrected adsorption data of nitrogen on samples 1, 2 and 3 at 77.8K.
the HILDA method, are remarkably similar. From the SED's in Figs. 4.17 and 4.18 shows that the high energy sites labelled A (from 12 to 15 kJmol\(^{-1}\)) decrease with increasing STPP coverage, while region B shows that the intermediate sites are similar for all the three samples. Region C (from 6 to 8 kJmol\(^{-1}\)) show the low energy sites increase with increasing coverage of STPP. Region D (below 6 kJmol\(^{-1}\)) has no monotonic trend.

This result is in accord with the comparison of HILDA and CAEDMON by House & Jaycock [1977] for a carbon sample known as Spheron 6. In that case, analysis of the data gave good general agreement, with the HILDA result showing some additional details.

### TABLE 4.14 Parameters for the CAEDMON Analysis for the N\(_2\) data at 77.8K

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of patches</th>
<th>r.m.s. (10^{-3})</th>
<th>Monolayer volume termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>4.85</td>
<td>MC</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>3.17</td>
<td>MC</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>4.52</td>
<td>MC</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>4.41</td>
<td>BET</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1.98</td>
<td>BET</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.75</td>
<td>BET</td>
</tr>
</tbody>
</table>
4.5. Adsorption of Ar, CO, Kr and N₂ onto the surface of barium sulphate

To characterize the surface of barium sulphate, four different adsorbates with the following properties: dipole moment (CO); quadrupole moment (N₂); and electrically neutral molecules (Ar and Kr) were used. From the adsorption isotherms, the specific surface area of barium sulphate was estimated with the four adsorbates. The heterogeneity analysis for the four adsorbates further examines the smoothing parameters; compares the multilayer correction and BET monolayer volume; the stability of the energy distributions; compares the minimum number of interactions required to obtain a site energy distribution. The above properties are compared with the Hill-de Boer and Langmuir models.

4.5.1. Isotherms

The surface of barium sulphate was probed with four different gases: argon, carbon monoxide, krypton and nitrogen by determining the adsorption isotherms at 77.8K. The relative pressure range measured for each gas is given in the table 4.15 below:

<table>
<thead>
<tr>
<th>GAS</th>
<th>RELATIVE PRESSURE RANGE</th>
<th>SATURATION VAPOUR PRESSURE/mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>4 x 10⁻⁶ - 0.7</td>
<td>1.76</td>
</tr>
<tr>
<td>Ar</td>
<td>5 x 10⁻⁸ - 1.0</td>
<td>219.48</td>
</tr>
<tr>
<td>CO</td>
<td>2.6 x 10⁻⁸ - 0.35</td>
<td>526.34</td>
</tr>
<tr>
<td>N₂</td>
<td>1.2 x 10⁻⁸ - 0.35</td>
<td>801.42</td>
</tr>
</tbody>
</table>
For this study, the isotherms were measured well above the monolayer region. The adsorption isotherms of CO and N\textsubscript{2} are presented in Figs. 4.19a, 4.19b and 4.19c, are seen to be type II. At low pressures, CO is adsorbed more strongly than N\textsubscript{2}, however the isotherms cross at a relative pressure of 0.115.

The isotherms of argon and krypton, shown in Figs. 4.20a and 4.20b, are again of type II, but show a very gradual uptake of gas at low pressures. Argon has a slightly greater initial rise than krypton, followed by a region of overlap and then stronger multilayer adsorption by argon.

The krypton isotherm shows no submonolayer steps in this work, although the adsorption temperature of krypton at 77.8K is below its two-dimensional critical temperature. House (1975) showed submonolayer steps in the adsorption of krypton onto the (100) faces of sodium chloride at 77.5K. This vertical "step" indicates the two-dimensional condensation process and may require a high degree of uniformity as for these (100) surfaces of the sodium chloride crystals. Argon and krypton adsorption isotherms on graphitised carbon blacks at 78K determined by many workers (Polly et. al (1953) and Singleton and Halsey (1954)) have found "steps", which were attributed to homogeneity of the graphitised carbon blacks. From this study, the krypton isotherms indicates that the surface of barium sulphate is very heterogeneous.
Fig. 4.19a Comparison of the nitrogen and carbon monoxide adsorption isotherms on sample 1 at 77.8K

Nitrogen

* Carbon monoxide

Amount adsorbed (mmolg⁻¹)

Relative pressure
Fig. 4.19b Comparison of the nitrogen and carbon monoxide adsorption isotherms on sample 1 at 77.8K
Fig. 4.19c Comparison of the nitrogen and carbon monoxide adsorption isotherms on sample 1 at 77.8K
Fig. 4.20a Comparison of the argon and krypton adsorption isotherms on sample 1 at 77.8K
Fig. 4.20b Comparison of the argon and krypton adsorption isotherms on sample 1 at 77.8K

- Argon
- Krypton

Relative pressure

Amount adsorbed (mmol g⁻¹)
No "steps" are expected for the other gases i.e. argon, carbon monoxide and nitrogen, as the adsorption temperature, 77.8K is well above their two-dimensional critical temperature.

Comparison of the nitrogen and argon adsorption isotherms show that nitrogen is more strongly adsorbed than argon. The trend at low pressures, below 1 mmHg, for the adsorption of the four gases on barium sulphate at 77.8K is CO > N₂ > Ar > Kr.

4.5.2. **Surface Area Analysis**

The isotherms were analysed using the BET method to estimate the specific surface area of barium sulphate. The BET plots are shown in Figs. 4.21, 4.22, 4.23, and 4.24, and the parameters calculated are given in Table 4.16. Table 4.17 shows the linear regression to this data. The line drawn in the BET plots was by hand, although the parameters used were from the computerised polynomial fit of degree 1. For the pressure range analysed using the BET method, the krypton data gives the best fit from the four gases employed. The spread of estimated specific surface areas of barium sulphate using the four gases is from 5.4 to 8.55 m² g⁻¹, with krypton and argon giving very similar values.

Emmett and De Witt (1941) estimated with N₂, the specific surface area to be 4.3 m² g⁻¹ for barium sulphate which is close to the Ar and Kr results in this study. Smith and Puddington (1960) estimated the specific surface area of a barium sulphate sample to be 18 m² g⁻¹ using nitrogen adsorption data but gave no details. Jopling (1952)
Fig. 4.21 Nitrogen BET plot for sample 1 at 77.8K
Fig. 4.22  Krypton BET plot for sample 1 at 77.8K
Fig. 4.23 Argon BET plot for sample 1 at 77.8K
Fig. 4.24 Carbon monoxide BET plot for sample 1 at 77.8K
### TABLE 4.16  Data from BET analysis for Sample 1 at 77.8K

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>RELATIVE PRESSURE RANGE</th>
<th>C</th>
<th>$E_1$ (kJ mol$^{-1}$)</th>
<th>$n$ (nm$^2$ molecule$^{-1}$)</th>
<th>$V_m$ (mmol g$^{-1}$)</th>
<th>$S$ (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>0.05 - 0.35</td>
<td>58.5</td>
<td>8.2</td>
<td>0.162</td>
<td>0.0887</td>
<td>8.65</td>
</tr>
<tr>
<td>CO</td>
<td>0.05 - 0.30</td>
<td>325.0</td>
<td>9.7</td>
<td>0.147</td>
<td>0.0746</td>
<td>6.60</td>
</tr>
<tr>
<td>Kr</td>
<td>0.05 - 0.25</td>
<td>102.0</td>
<td>12.4</td>
<td>0.195</td>
<td>0.0464</td>
<td>5.45</td>
</tr>
<tr>
<td>Ar</td>
<td>0.06 - 0.31</td>
<td>98.0</td>
<td>9.3</td>
<td>0.169</td>
<td>0.0533</td>
<td>5.42</td>
</tr>
</tbody>
</table>

### TABLE 4.17  Regression analysis to BET data for Sample 1 at 77.8K

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>CORRELATION COEFFICIENT</th>
<th>RMS</th>
<th>INTERCEPT</th>
<th>SLOPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>0.994</td>
<td>0.0025</td>
<td>0.0086</td>
<td>0.494</td>
</tr>
<tr>
<td>CO</td>
<td>0.9993</td>
<td>0.0016</td>
<td>0.0018</td>
<td>0.596</td>
</tr>
<tr>
<td>Kr</td>
<td>0.9998</td>
<td>0.0009</td>
<td>0.0094</td>
<td>0.951</td>
</tr>
<tr>
<td>Ar</td>
<td>0.9991</td>
<td>0.0039</td>
<td>0.0085</td>
<td>0.828</td>
</tr>
</tbody>
</table>
found specific surface areas from dye adsorption which varied from 1.0 to 7.6 $m^2g^{-1}$. Thus the specific surface area of barium sulphate varies within the literature, but the total spread including the current results, is not substantial.

From the solution adsorption isotherm of STPP on barium sulphate, taking the molecular cross-section area of STPP from the work of Miura (1963) as 0.37 nm$^2$ molec$^{-1}$ and the monolayer volume ($V_m$) as the plateau region, the specific surface area estimated was approximately 5.06 $m^2g^{-1}$. In addition, the solution adsorption isotherm data was fitted to the Langmuir model, and the estimated $V_m$ was 0.0256 mmolg$^{-1}$. Using this $V_m$, the specific surface area was calculated as 5.7 $m^2g^{-1}$. These results are in agreement with the Ar and Kr results.

4.5.3. Heterogeneity Analysis
4.5.3.1. Smoothing

The parameters obtained from the heterogeneity analysis are presented in Table 4.18 for $N_2$, Table 4.19 for CO, Table 4.20 for Kr and Table 4.21 for Ar.

The smoothing factor $SM_1$ is constant for each adsorbate, since the dataset routine was applied to the raw data once. The $SM_2$ values are larger for the Langmuir model compared to the Hill-de Boer model or the Fowler-Guggenheim model for each adsorbate. The rms results for each adsorbate studied, show that the Hill-de Boer and Fowler-Guggenheim model fits better to the data compared to the Langmuir model.
### Table 4.18: The results of the HILDA analysis for barium sulphate 1 at 77.8K

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>NUMBER OF DATA POINTS</th>
<th>MODEL</th>
<th>MULTILAYER CORRECTION</th>
<th>NUMBER OF ITERATIONS</th>
<th>r.m.s.</th>
<th>SM1</th>
<th>SM2</th>
<th>Vm /mmolg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>153</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0137</td>
<td>0.0011</td>
<td>0.0168</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>153</td>
<td>HdB</td>
<td>NO</td>
<td>44</td>
<td>0.0107</td>
<td>0.0011</td>
<td>0.0055</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>144</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0091</td>
<td>0.0012</td>
<td>0.0094</td>
<td>0.0861</td>
</tr>
<tr>
<td>N₂</td>
<td>153</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3256</td>
<td>0.0011</td>
<td>0.1426</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>144</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.3019</td>
<td>0.0012</td>
<td>0.1445</td>
<td>0.0861</td>
</tr>
<tr>
<td>N₂</td>
<td>153 (RANDOMISED)</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0112</td>
<td>0.0012</td>
<td>0.0115</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>153 (RANDOMISED)</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3037</td>
<td>0.0012</td>
<td>0.2249</td>
<td>0.2164</td>
</tr>
<tr>
<td>ADSORBATE</td>
<td>NUMBER OF DATA POINTS</td>
<td>MODEL</td>
<td>MULTILAYER CORRECTION</td>
<td>NUMBER OF ITERATIONS</td>
<td>r.m.s.</td>
<td>SM1</td>
<td>SM2</td>
<td>Vm/mmol g⁻¹</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------</td>
<td>--------</td>
<td>------------------------</td>
<td>----------------------</td>
<td>--------</td>
<td>-------</td>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>CO</td>
<td>115</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0033</td>
<td>0.0009</td>
<td>0.0015</td>
<td>0.0957</td>
</tr>
<tr>
<td>CO</td>
<td>111</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0030</td>
<td>0.0009</td>
<td>0.0013</td>
<td>0.0751</td>
</tr>
<tr>
<td>CO</td>
<td>115</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.1615</td>
<td>0.0009</td>
<td>0.0171</td>
<td>0.0957</td>
</tr>
<tr>
<td>CO</td>
<td>111</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.1629</td>
<td>0.0009</td>
<td>0.0185</td>
<td>0.0751</td>
</tr>
<tr>
<td>ADSORBATE</td>
<td>NUMBER OF DATA POINTS</td>
<td>MODEL</td>
<td>MULTILAYER CORRECTION</td>
<td>NUMBER OF ITERATIONS</td>
<td>r.m.s.</td>
<td>SM1</td>
<td>SM2</td>
<td>Vm /mmolg$^{-1}$</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------</td>
<td>-------</td>
<td>-----------------------</td>
<td>----------------------</td>
<td>--------</td>
<td>-------</td>
<td>-------</td>
<td>------------------</td>
</tr>
<tr>
<td>Kr</td>
<td>87</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0009</td>
<td>0.0007</td>
<td>0.0002</td>
<td>0.0812</td>
</tr>
<tr>
<td>Kr</td>
<td>62</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0005</td>
<td>0.0007</td>
<td>0.0002</td>
<td>0.0442</td>
</tr>
<tr>
<td>Kr</td>
<td>87</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.1182</td>
<td>0.0007</td>
<td>0.0099</td>
<td>0.0812</td>
</tr>
<tr>
<td>Kr</td>
<td>62</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.1160</td>
<td>0.0007</td>
<td>0.0067</td>
<td>0.0442</td>
</tr>
<tr>
<td>Kr</td>
<td>87</td>
<td>FG</td>
<td>NO</td>
<td>15</td>
<td>0.0011</td>
<td>0.0007</td>
<td>0.0002</td>
<td>0.0812</td>
</tr>
<tr>
<td>Kr</td>
<td>62</td>
<td>FG</td>
<td>YES</td>
<td>15</td>
<td>0.0006</td>
<td>0.0007</td>
<td>0.0002</td>
<td>0.0442</td>
</tr>
<tr>
<td>ADSORBATE</td>
<td>NUMBER OF DATA POINTS</td>
<td>MODEL</td>
<td>MULTILAYER CORRECTION</td>
<td>NUMBER OF ITERATIONS</td>
<td>r.m.s.</td>
<td>SM1</td>
<td>SM2</td>
<td>$V_m$ /mmolg$^{-1}$</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------</td>
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<td>----------------------</td>
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<td>-----</td>
<td>------------------</td>
</tr>
<tr>
<td>Ar</td>
<td>99</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0065</td>
<td>0.0025</td>
<td>0.0013</td>
<td>0.1572</td>
</tr>
<tr>
<td>Ar</td>
<td>84</td>
<td>HdB</td>
<td>YES</td>
<td>7</td>
<td>0.0016</td>
<td>0.0027</td>
<td>0.0003</td>
<td>0.0527</td>
</tr>
<tr>
<td>Ar</td>
<td>99</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.0824</td>
<td>0.0025</td>
<td>0.0050</td>
<td>0.1572</td>
</tr>
<tr>
<td>Ar</td>
<td>84</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>12</td>
<td>0.0309</td>
<td>0.0027</td>
<td>0.0012</td>
<td>0.0527</td>
</tr>
</tbody>
</table>
4.5.3.2. **Multilayer Correction**

Comparison of the monolayer volumes for each adsorbate determined by the BET method and the multilayer correction method are given in Table 4.22.

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>MONOLAYER VOLUME/mmolg⁻¹</th>
<th>BET</th>
<th>MULTILAYER CORRECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.0887</td>
<td>0.0861</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.0746</td>
<td>0.0751</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>0.0464</td>
<td>0.0442</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>0.0533</td>
<td>0.0527</td>
<td></td>
</tr>
</tbody>
</table>

The values of the monolayer volumes are slightly smaller for N₂, Kr and Ar from the multilayer corrected method, except for CO, but the values are remarkably close for the two methods. Similar results for the two methods have been obtained by House (1984) for N₂ on chemically modified silica.

4.5.3.3. **Stability of SED**

The SED's were determined using the HILDA method for the four gases. The nitrogen adsorption data was used to examine the stability of the SED obtained from the HILDA method. The isotherm coverage data was randomised by a Random number generator within the limits of ± 1% deviation. The SED was determined again using the Hill-de Boer model in the HILDA method. The results for the full range of data is shown in Fig. 4.25, however, Fig. 4.26 was plotted which gives a detailed SED above 5.0 kJmol⁻¹. Both the randomised and unrandomised SEDs are identical in structure.
Fig. 4.25 The site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of nitrogen on sample 1 at 77.8K.

Original

---

1% randomized
Fig. 4.26  Detailed plot of the site energy distributions from Fig. 4.25 above 5kJmol$^{-1}$
This procedure was applied to the analysis of the nitrogen data in terms of the Langmuir model for the adsorption at fixed surface energy. The SED's obtained are shown in Fig. 4.27, and again are identical.

The results show that the SED's calculated are not dependent on particular configurations of measured data points on the isotherm, and that the smoothing routines are effectively eliminating the contribution of experimental scatter on the isotherms. In fact, the data presented tends to be over smoothed to show the dominant features in the energy distribution rather than aim for maximum information with risk of inclusion of the effects of "noise".

4.5.3.4. Minimum Number of Iterations

The number of iterations required within the HILDA method to obtain the best fit to the smooth isotherm was allowed to continue up to 44 iterations. This was compared with 15 iterations, see Fig. 4.28 for the Hill-de Boer model. The rms for the 15 iterations and 44 iterations was $1.37 \times 10^{-2}$ and $1.07 \times 10^{-2}$, respectively. Both the 15 and 44 iterated SED's visually appear identical.

The SED's obtained for the Langmuir model under these conditions are shown in Fig. 4.29, and again show close agreement.

The maximum number of iterations was limited within the HILDA method to 15 in this study.
Fig. 4.27 The site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of nitrogen on sample 1 at 77.8K.
Fig. 4.28 The site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of nitrogen on sample 1 at 77.8K

15 Iterations

44 Iterations
Fig. 4.29 The site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of nitrogen on sample 1 at 77.8K.
4.5.3.5. Energy Distributions

The SED results of the nitrogen data have been presented earlier in this chapter, and are now compared with those for CO. Fig. 4.30 shows SEDs for CO for the Hill-de Boer model, with and without the multilayer correction. Two prominent features are seen at high energy sites (i.e. 12.6 to 14.3 kJmol\(^{-1}\)) and low energy sites (i.e. 4.5 to 7.7 kJmol\(^{-1}\)).

The multilayer correction has reduced the contribution near the monolayer, and a corresponding increase at higher energies occurs due to the normalisation of the energy distribution.

Similar results are shown by the Langmuir model in Fig. 4.31.

The multilayer corrected EDs of nitrogen and CO determined from the Hill-de Boer model were compared, see Fig. 4.32. Since the Ln Å value for each adsorbate (in this case N\(_2\) and CO) was estimated at 77.8K; the energy scale for each SED as shown in Fig. 4.32 is also an estimate. However, if we assume that both the SED's are aligned at the monolayer, irrespective of the energy scale, then a reasonable comparison can be made between the two SED’s, see Fig. 4.33.

The N\(_2\) and CO SED's show very similar features, the two most prominent features are the high energy sites, 11.7 to 14.3 kJmol\(^{-1}\) and the low energy sites, 4.0 to 6.7 kJmol\(^{-1}\). The high energy sites are much more prominent in the CO SED's and the low energy sites are much more prominent in the N\(_2\) SED. Similar results were obtained when the Langmuir model was utilised, see Fig. 4.34.
Fig. 4.30 Comparison of the original and multilayer corrected site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of carbon monoxide on sample 1 at 77.8K.
Fig. 4.31 Comparison of the original and multilayer corrected site-energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of carbon monoxide on sample 1 at 77.8 K.
Fig. 4.32 Comparison of the multilayer corrected site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of nitrogen and carbon monoxide on sample 1 at 77.8K.

![Graph showing the comparison of multilayer corrected site energy distribution functions for nitrogen and carbon monoxide.](image)
Fig. 4.33 Alignment of the site energy distribution functions from Fig. 4.32 at the multilayer corrected monolayer volume

\[ F(U) \text{ (mol kJ}^{-1}\text{)} \]

Nitrogen

Carbon monoxide
Fig. 4.34 Comparison of the multilayer corrected site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of nitrogen and carbon monoxide on sample I at 77.8K, aligned at the multilayer corrected monolayer volume.
The SED's of argon are presented in Fig. 4.35 for the Hill-de Boer model, and a detailed plot in Fig. 4.36 for the full data and the multilayer corrected data, respectively. The results show that argon interacts with the midrange (i.e. 8 to 10 kJmol\(^{-1}\)) and low energy (5.5 to 7.0 kJmol\(^{-1}\)) sites. This was found to be the case with the Langmuir model SED's, see Figs. 4.37, 4.38, and 4.39.

The multilayer corrected SED's of N\(_2\) and Ar were aligned at the monolayer and compared. Fig. 4.40 shows the Hill-de Boer model results and Fig. 4.41 shows the Langmuir model results. Both N\(_2\) and Ar interact strongly with the low energy sites, 4.3 to 6.2 kJmol\(^{-1}\), on the surface of barium sulphate, however, only N\(_2\) interacts strongly with the high energy sites, 12.0 - 14.3 kJmol\(^{-1}\).

The multilayer corrected data for krypton was analysed using the Hill-de Boer, Fowler-Guggenheim and the Langmuir model. These results are plotted in Fig. 4.42. The Langmuir model SED was aligned by translating the SED by 6.0 kJmol\(^{-1}\) to the Hill-de Boer and Fowler-Guggenheim model SED's, see Fig. 4.43. Since the difference between the Fowler-Guggenheim and Langmuir model is that the former takes lateral interactions into consideration, while the latter model does not. Therefore, 6.0 kJmol\(^{-1}\) may be the lateral interaction energy of krypton atoms on the surface of barium sulphate.

The Hill-de Boer and Fowler-Guggenheim give virtually identical SED's, and the Langmuir model SED has the same features as the other two models but seems "stretched".
Fig. 4.35 Comparison of the original with the multilayer corrected site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of argon on sample 1 at 77.8K.

Original

--- --- --- Multilayer corrected
Fig. 4.36 Detailed plot of the site energy distribution functions from Fig. 4.35 above 5kJ mol\(^{-1}\)
Fig. 4.37 Comparison of the original with the multilayer corrected site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of argon on sample 1 at 77.8K.
Fig. 4.38 Detailed plot of the site energy distribution functions from Fig. 4.37 above 10kJmol⁻¹

Original --- Multilayer corrected

\[ F(U) \text{ (mol kJ}^{-1}) \]

\[ U \text{ (kJ mol}^{-1}) \]
Fig. 4.39 Comparison of the multilayer corrected site energy distributions for the Hill-de Boer (Fig. 4.36) and Langmuir models (Fig. 4.38)
Fig. 4.40 Comparison of the multilayer corrected site energy distribution functions from Fig. 4.7c and Fig. 4.36 for sample 1 aligned at the multilayer corrected monolayer volume.

\[ \begin{align*}
&\text{Nitrogen} & \text{Argon} \\
&0.50 & 0.45 \\
&0.40 & 0.35 \\
&0.30 & 0.25 \\
&0.20 & 0.15 \\
&0.10 & 0.05 \\
&0.00 & \\
\end{align*} \]

\[ \begin{align*}
&U (\text{kJ mol}^{-1}) \\
&4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 \\
& & & & & & & & & & & & \\
\end{align*} \]
Fig. 4.41 Comparison of the multilayer corrected site energy distribution functions from Fig. 4.8c and Fig. 4.38 for sample 1 aligned at the multilayer corrected monolayer volume.

Nitrogen

Argon
Fig. 4.42 The multilayer corrected site energy distribution functions obtained by HILDA from the Hill-de Boer, Langmuir and Fowler-Guggenheim analysis of the adsorption of krypton on sample 1 at 77.8K
Fig. 4.43 Showing the alignment of the Langmuir with the Hill-de Boer and Fowler-Guggenheim model site energy distributions for krypton on sample 1 at 77.8K.
The krypton SED's were compared with argon. Figs. 4.43a and 4.44 shows the aligned multilayer corrected SED's calculated with the Hill-de Boer and Langmuir models, respectively. The results indicate the krypton interacts with the majority of midrange energy sites compared to argon which interacts much strongly with the low energy sites.
Fig. 4.43a Alignment of the site energy distribution functions from Fig. 4.38 and Fig. 4.43 at the multilayer corrected monolayer volume.

The graph shows the distribution of site energies for Argon and Krypton. The energy is plotted on the x-axis as $U$ (kJmol$^{-1}$), and the distribution function $F(U)$ (molkJ$^{-1}$) is plotted on the y-axis. The solid line represents Argon, and the dashed line represents Krypton.
Fig. 4.44 Alignment of the site energy distribution functions from Fig. 4.37 and Fig. 4.42 at the multilayer corrected monolayer volume.

![Graph showing the alignment of site energy distribution functions for Argon and Krypton.](image)
4.6. Comparison of Samples 1 and 4

Two samples of precipitated barium sulphate were examined using the Heterogeneity Analysis. Both samples were prepared by the procedure given in Chapter 3. Sample 1 was prepared by the author while the other barium sulphate, sample 4, had been previously prepared at Unilever Research, Port Sunlight (Smith, 1982).

4.6.1. Isotherms

$N_2$ and Kr gases were used to probe the surfaces of the two samples to give the isotherms and the HILDA SED's; the specific surface was estimated from the Kr data. The $N_2$ isotherms are represented in Figs. 4.45 and 4.46. Sample 1 adsorbs $N_2$ more strongly than sample 4 in the pressure range studied, however, the $N_2$ surface areas are not obtainable as the adsorption is well below the monolayer.

The shapes of the isotherms show that sample 4 has a much steeper rise and a flatter plateau region than sample 1 in the pressure range.

The Kr isotherms are shown in Figs. 4.47 and 4.48 and include the multilayer region. As is often observed, the initial rise is less steep than for $N_2$ and again, sample 4 has the sharper rise.

4.6.2. Estimation of surface area

The Kr isotherms were used to estimate the specific surface area of sample 1 and 4 with the BET model. The BET plot is shown in Fig. 4.48a for sample 4. The results of the BET analysis is given in the Table 4.23 below:
Fig. 4.45 Adsorption isotherms of nitrogen on samples 1 and 4 at 77.8K

Sample 4

Sample 1

Amount adsorbed (mmol g\(^{-1}\))

Relative pressure
Fig. 4.46 Adsorption isotherms of nitrogen on samples 1 and 4 at 77.8K.
Fig. 4.47 Adsorption isotherms of krypton on samples 1 and 4 at 77.8K
Fig. 4.48 Adsorption isotherms of krypton on samples 1 and 4 at 77.8K
FIGURE 4.48a BET plot of krypton at 77.8K
TABLE 4.23 BET Analysis of Kr Data at 77.8K

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>RELATIVE PRESSURE RANGE</th>
<th>C</th>
<th>E₀</th>
<th>σ₀</th>
<th>V_m</th>
<th>S</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>0.05 - 0.25</td>
<td>102</td>
<td>12.4</td>
<td>0.195</td>
<td>0.0464</td>
<td>5.45</td>
</tr>
<tr>
<td>4</td>
<td>0.028 - 0.17</td>
<td>351.4</td>
<td>13.2</td>
<td>0.195</td>
<td>0.0132</td>
<td>1.55</td>
</tr>
</tbody>
</table>

The polynomial fit of degree 1 parameters are given in the Table below:

TABLE 4.24 Parameters from linear regression analysis for Kr Data at 77.8K

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CORRELATION COEFFICIENT</th>
<th>r.m.s.</th>
<th>INTERCEPT</th>
<th>SLOPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9998</td>
<td>0.0009</td>
<td>0.0094</td>
<td>0.9512</td>
</tr>
<tr>
<td>4</td>
<td>0.9998</td>
<td>0.0028</td>
<td>0.0096</td>
<td>3.363</td>
</tr>
</tbody>
</table>

Table 4.24 shows that the BET model fitted better to the krypton data for sample 1 than sample 4. The intercept from the BET analysis are very similar but the slopes vary considerably which will dominate in the calculation of the specific surface area.

Table 4.23 shows that the BET 'C' constant for sample 4 is much larger than that for sample 1, as expected from the isotherm shapes. The adsorption energy of the first layer, $E_1$, is very similar for both samples. The specific surface area of sample 1 is approximately 3.5 times larger than that of sample 4; this trend was reflected in the particle size, as sample 4 had a larger particle size compared to sample 1. Cuming and Schulman (1959) estimated the
specific surface area of approximately 0.1 m$^2$g$^{-1}$ using krypton (molecular cross-sectional area of 0.20 nm$^2$molec$^{-1}$) as the adsorbate on barium sulphate.

4.6.3. **Heterogeneity Analysis**

4.6.3.1. **Smoothing**

The smoothing parameters obtained from the HILDA method are given in Table 4.25. The SM1 values for the individual adsorbate are the same suggesting that dataset fits the smooth curve identically to both the raw isotherm data. The rms for the Hill-de Boer model is much smaller compared to the Langmuir model for each adsorbate. For the krypton results, the SM2 values for the Hill-de Boer model are smaller compared to the Langmuir model.

4.6.3.2. **Comparison of $V_m$**

The monolayer volumes, $V_m$, determined from the BET model and the multilayer correction are given in the Table 4.26 below:

<table>
<thead>
<tr>
<th>TABLE 4.26</th>
<th>Kr Monolayer volumes from the BET and multilayer correction method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_m$/mmolg$^{-1}$</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>BET</td>
</tr>
<tr>
<td>1</td>
<td>0.0464</td>
</tr>
<tr>
<td>4</td>
<td>0.0132</td>
</tr>
</tbody>
</table>

The $V_m$ from the multilayer corrected method is slightly lower than from the BET model for both samples, however very good agreement is observed.
### TABLE 4.25 The results of the HILDA analysis for barium sulphate 4 at 77.8K

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>NUMBER OF DATA POINTS</th>
<th>MODEL</th>
<th>MULTILAYER CORRECTION</th>
<th>NUMBER OF ITERATIONS</th>
<th>r.m.s.</th>
<th>SM1</th>
<th>SM2</th>
<th>Vm/ mmolg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>91</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0012</td>
<td>0.0013</td>
<td>0.0003</td>
<td>0.0120</td>
</tr>
<tr>
<td>N₂</td>
<td>91</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.0375</td>
<td>0.0013</td>
<td>0.0008</td>
<td>0.0120</td>
</tr>
<tr>
<td>Kr</td>
<td>87</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0008</td>
<td>0.0010</td>
<td>0.0003</td>
<td>0.0178</td>
</tr>
<tr>
<td>Kr</td>
<td>64</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0006</td>
<td>0.0011</td>
<td>0.0002</td>
<td>0.0129</td>
</tr>
<tr>
<td>Kr</td>
<td>87</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>14</td>
<td>0.2151</td>
<td>0.0010</td>
<td>0.0071</td>
<td>0.0178</td>
</tr>
<tr>
<td>Kr</td>
<td>64</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>14</td>
<td>0.1955</td>
<td>0.0011</td>
<td>0.0039</td>
<td>0.0129</td>
</tr>
</tbody>
</table>
4.6.4. **Nitrogen data**

The nitrogen isotherms were used to determine the SEDs by the HILDA method using the Hill-de Boer model. Fig. 4.49 shows the SED's that have been normalised at 1 mmHg. Both the SED's show that sample 1 and 4 are very heterogeneous. The features within the SED for both samples are very similar suggesting that this may be the characteristic SED for barium sulphate i.e like a "fingerprint". The SED of sample 4 ends at 15.2 kJmol\(^{-1}\), but for sample 1 it ends at 14.3 kJmol\(^{-1}\). This would suggest that the surfaces of sample 1 and 4 may have further higher energy sites present. To study these higher energy sites would require isotherm data at lower pressures than 10\(^{-5}\) mmHg. Both SED's have the same number of peaks, the peak height ratio within the SED is shown in the Table below:

<table>
<thead>
<tr>
<th>TABLE 4.27. Peak Height Ratio from Fig. 4.49</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

The peak area under the individual regions are given in Table 4.28. Both the peak height ratio and area of the individual region show differences between the two SED's which is not clear by observation alone of Fig. 4.49.

Table 4.28 indicates that region A for sample 4 represents approximately 3/5 of the surface compared with 1/3 for sample 1. Thus, the surface of sample 4 has 4/15 more of these high energy sites present.
Fig. 4.49 The site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of nitrogen on samples 1 and 4 at 77.8K (normalized).
TABLE 4.28  Peak Areas Determined from the Site Energy Distributions in Fig 4.49

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PEAK A AREA</th>
<th>PEAK B AREA</th>
<th>PEAK C AREA</th>
<th>PEAK D AREA</th>
<th>PEAK E AREA</th>
<th>TOTAL PEAK AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.5678</td>
<td>0.068</td>
<td>0.0988</td>
<td>0.0799</td>
<td>0.0555</td>
<td>0.0688 7.18 0.9576</td>
</tr>
<tr>
<td>1</td>
<td>0.3252</td>
<td>0.1514</td>
<td>0.1222</td>
<td>0.1529</td>
<td>0.1052</td>
<td>0.1284 13.03 0.9853</td>
</tr>
</tbody>
</table>

TABLE 4.29  Peak Areas Determined from the Site Energy Distributions in Fig 4.50

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PEAK A AREA</th>
<th>PEAK B AREA</th>
<th>PEAK C AREA</th>
<th>PEAK D AREA</th>
<th>PEAK E AREA</th>
<th>TOTAL PEAK AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.6236</td>
<td>-</td>
<td>0.0884</td>
<td>0.0745</td>
<td>0.1842</td>
<td>0.9707</td>
</tr>
<tr>
<td>1</td>
<td>0.3433</td>
<td>0.0993</td>
<td>0.0175</td>
<td>0.2176</td>
<td>0.2840</td>
<td>0.9617</td>
</tr>
</tbody>
</table>
The normalised nitrogen data was analysed using the Langmuir model. Fig. 4.50 shows the SED's obtained for sample 1 and 4. The structure of the Langmuir model SED have distinct features compared to the Hill-de Boer model.

As with the Hill-de Boer model SED's, the Langmuir model SED's also show that the surface of sample 4 has higher energy site present (i.e above 18.0 kJmol$^{-1}$) than sample 1. The SED of sample 4 does not have region B present. The area of individual regions within the SED's are given in Table 4.29.

The area of the high energy sites for sample 4 is approximately 28% larger than for sample 1. The average energy for region C is 14.8 kJmol$^{-1}$ for sample 1 and 15.3 kJmol$^{-1}$ for sample 4.

Both the N$_2$ SED's from the Hill-de Boer and Langmuir model show that the surface of sample 4 has a larger proportion of high energy sites compared to sample 1.

4.6.5. Krypton data

The krypton isotherm was analysed using the HILDA method for sample 1 and 4. The Hill-de Boer model was used and the SED's are shown in Fig. 4.51. The shape of the SED for sample 1 is an exponential decay whereas, for sample 4 a broad peak is found in the middle of the SED i.e between 10.6 and 11.7 kJmol$^{-1}$. The steep rise at approximately 8.0 kJmol$^{-1}$ is due to the formation of multilayers.
Fig. 4.50 The site energy distribution obtained by HILDA from the Langmuir analysis of the adsorption of nitrogen on samples 1 and 4 at 77.8K (normalized)
Fig. 4.51 The site energy distribution functions obtained by the HILDA from the Hill-de Boer analysis of the adsorption of krypton on samples 1 and 4 at 77.8K.
The multilayer correction was applied to the krypton data. The SED's obtained for this data is shown in Fig. 4.52. The regions are labelled from A to F with subscripts representing the sample. Both the SED's indicate that the surfaces of sample 1 and 4 are very heterogeneous and have the same number of features. Region C is prominent for sample 4 but sample 1 does not have a distinct prominent feature.

The area under the individual regions for both the SED's are given in Table 4.30. From the table, the area of regions A, B, D and E for both samples are very similar. However, region C for sample 4 is 11.2% greater than that of sample 1, while for region F, sample 1 is 8% greater than for sample 4.

The Langmuir model was used to determine the SED's for the krypton data for sample 1 and 4, see Fig. 4.53.

The steep rise at approximately 14.0 kJmol$^{-1}$ is due to the formation multilayers. To examine this SED in detail, from 14.0 to 20.0 kJmol$^{-1}$, Fig. 4.54 was plotted. This shows 4 distinct regions for sample 4 and 5 regions for sample 1. The regions are labelled from A to E with the subscript representing the sample. Region B$_4$ is either not present or is a part of region A$_4$, but it is difficult to distinguish. This was also observed in the Langmuir SED of N$_2$ for sample 4, see Fig. 4.50.

To the krypton data the multilayer correction was applied and the Langmuir model SED's obtained are represented in Fig. 4.55. Sample 1 has 6 regions and sample 4 has 5 regions. The regions were labelled
Fig. 4.52 Application of the multilayer correction to the site energy distributions shown in Fig. 4.51
### TABLE 4.30  Peak Areas Determined From SED's in Fig 4.52

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PEAK A AREA</th>
<th>PEAK A %</th>
<th>PEAK B AREA</th>
<th>PEAK B %</th>
<th>PEAK C AREA</th>
<th>PEAK C %</th>
<th>PEAK D AREA</th>
<th>PEAK D %</th>
<th>PEAK E AREA</th>
<th>PEAK E %</th>
<th>PEAK F AREA</th>
<th>PEAK F %</th>
<th>TOTAL PEAK AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.1839</td>
<td>18.61</td>
<td>0.1321</td>
<td>13.37</td>
<td>0.2922</td>
<td>29.57</td>
<td>0.2046</td>
<td>20.71</td>
<td>0.1462</td>
<td>14.80</td>
<td>0.0291</td>
<td>2.94</td>
<td>0.9882</td>
</tr>
<tr>
<td>1</td>
<td>0.1961</td>
<td>20.00</td>
<td>0.1195</td>
<td>12.19</td>
<td>0.1801</td>
<td>18.37</td>
<td>0.2329</td>
<td>23.75</td>
<td>0.1445</td>
<td>14.74</td>
<td>0.1073</td>
<td>10.94</td>
<td>0.9806</td>
</tr>
</tbody>
</table>

### TABLE 4.31  Peak Areas Determined From SED's in Fig 4.55

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PEAK A AREA</th>
<th>PEAK A %</th>
<th>PEAK B AREA</th>
<th>PEAK B %</th>
<th>PEAK C AREA</th>
<th>PEAK C %</th>
<th>PEAK D AREA</th>
<th>PEAK D %</th>
<th>PEAK E AREA</th>
<th>PEAK E %</th>
<th>PEAK F AREA</th>
<th>PEAK F %</th>
<th>TOTAL PEAK AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.2105</td>
<td>20.95</td>
<td>-</td>
<td>-</td>
<td>0.4350</td>
<td>43.27</td>
<td>0.1664</td>
<td>16.55</td>
<td>0.1495</td>
<td>14.87</td>
<td>0.0438</td>
<td>4.36</td>
<td>1.6047</td>
</tr>
<tr>
<td>1</td>
<td>0.1463</td>
<td>14.60</td>
<td>0.1553</td>
<td>15.50</td>
<td>0.1464</td>
<td>14.61</td>
<td>0.1512</td>
<td>15.09</td>
<td>0.2639</td>
<td>26.34</td>
<td>0.1389</td>
<td>13.86</td>
<td>1.6017</td>
</tr>
</tbody>
</table>
Fig. 4.53 The site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of krypton on samples 1 and 4 at 77.8K.
Detailed plot of the site energy distributions from Fig. 4.53 above 14kJmol⁻¹

Fig. 4.54
Fig. 4.55 Site energy distribution functions from Fig. 4.53 with the application of the multilayer correction.
from A to F with subscript representing the sample. Application of the multilayer correction has enlarged the area of peak C₄, reduced the peak height and area of D₁ and given an additional feature, region F, found in both SEDs. Region B cannot be distinguished from region A for sample 4.

The area under the individual regions are presented in Table 4.31. The area of regions A, B, C, D and F are very similar for sample 1, but region E being the prominent feature has the largest area. For sample 4, region C represents the largest area. Since region A₄ may include a small proportion of region B₄, then regions A₄, D₄ and E₄ have approximately similar area, but region F₄ has a small area.

The Hill-de Boer model and Langmuir model for the krypton SED's show that sample 4 has a high proportion of mid-range energy sites but sample 1 has a broad range of surface sites.
4.7. **Effect of Adsorption Temperature**

The effect of adsorption temperature was investigated to study the sensitivity of the heterogeneity analysis with respect to the Hill-de Boer and Langmuir models. Furthermore, this data was used to determine the isomeric heat of adsorption using the Clausius-Claperyon equation. Also from this data, the molecular cross-sectional areas were estimated assuming that the surface area of barium sulphate remains constant at different adsorption temperatures.

4.7.1. **Isotherms of \( \text{N}_2 \)**

Adsorption isotherms of nitrogen on barium sulphate (sample 1) were determined at 77.8K, 80.8K and 81.6K. Figs. 4.56a, 4.56b, and 4.56c, show the three isotherms obtained. The relative pressure ranges for each isotherm is shown in the Table 4.32 below:

<table>
<thead>
<tr>
<th>TEMPERATURE/K</th>
<th>SATURATION VAPOUR PRESSURE/mmHg</th>
<th>RELATIVE PRESSURE RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>78.8</td>
<td>801.42</td>
<td>1.25 x 10^{-8} - 1.00</td>
</tr>
<tr>
<td>80.8</td>
<td>1120.69</td>
<td>8.95 x 10^{-9} - 0.60</td>
</tr>
<tr>
<td>81.6</td>
<td>1220.08</td>
<td>8.20 x 10^{-9} - 0.60</td>
</tr>
</tbody>
</table>

All three isotherms are of type II. The 80.8K and 81.6K isotherms at high pressure show more experimental scatter than the 77.8K isotherm.
Fig. 4.56a Adsorption isotherms of nitrogen on sample 1 at 77.8, 80.8 and 81.6K.

At 77.8K

At 80.8K

At 81.6K

Relative pressure

Amount adsorbed (mmol g\(^{-1}\))
Fig. 4.56b Adsorption isotherms of nitrogen on samples 1 at 77.8, 80.8 and 81.6K

At 77.8K

* At 80.8K

△ At 81.6K

Amount adsorbed (mmol/g)

Relative pressure

0.000 0.0001 0.0002 0.0003 0.0004 0.0005 0.0006 0.0007 0.0008 0.0009 0.0010 0.0011 0.0012 0.0013
Fig. 4.56c  Adsorption isotherms of nitrogen on sample 1 at 77.8, 80.8 and 81.6K
4.7.2. Estimation of $\sigma_0$

The specific surface area of barium sulphate was estimated from the 77.8K isotherm earlier (see section 4.1.2) and was found to be 8.65 m$^2$g$^{-1}$. The BET model was used to estimate the monolayer volume and the BET 'C' constant for the 80.8K and 81.6K isotherms. The BET plots are shown in Fig. 4.57. The parameters were then used to calculate the molecular cross-sectional area of nitrogen at 80.8K assuming constant surface area. The results are presented in Table 4.33.

<table>
<thead>
<tr>
<th>TEMPERATURE/K</th>
<th>RELATIVE PRESSURE RANGE</th>
<th>$E_1$ kJmol$^{-1}$</th>
<th>$V_m$ nmolg$^{-1}$</th>
<th>$\sigma_0$ nm$^2$molec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.8</td>
<td>0.05 - 0.35</td>
<td>58.5</td>
<td>8.2</td>
<td>0.0887</td>
</tr>
<tr>
<td>80.8</td>
<td>0.051 - 0.35</td>
<td>219.6</td>
<td>9.2</td>
<td>0.0551</td>
</tr>
<tr>
<td>81.6</td>
<td>0.07 - 0.35</td>
<td>350.3</td>
<td>9.6</td>
<td>0.0503</td>
</tr>
</tbody>
</table>

The molecular cross-sectional area of the $N_2$ molecule increases with increasing adsorption temperature on the surface of barium sulphate. The BET 'C' constant increase dramatically from 77.8K to 80.8K, but increases gradually from 80.8K to 81.6K. However, the adsorption energy of the first layer $E_1$ follows the same trends as the BET 'C' constants. McClellan and Harnsberg (1967) tabulated molecular cross-sectional area of various absorbates and showed that the size of the adsorbed molecule is not constant but varies with the adsorbent and temperature of adsorption.
Fig. 4.57 Nitrogen BET plots for Sample 1

At 77.8K

At 80.8K

At 81.6K

Relative pressure

\[ \frac{p}{v(p_0, p)} \]
4.7.3. **Isosteric Heat**

The isosteric heat, $\Delta H_{iso}$ of adsorption was estimated from the three isotherms, since:

$$
\left[ \frac{\partial (\ln P)}{\partial T} \right]_{n_a} = \left[ \frac{\partial (\ln P)}{\partial (1/T)} \right]_\theta = \frac{\Delta H_{iso}}{RT^2}
$$

where $P$ is the equilibrium pressure in mmHg, $T$ is the absolute temperature in Kelvins, $n_a$ is the amount adsorbed in mmolg$^{-1}$, and $R$ is the gas constant. This equation was used to drive $\Delta H_{iso}$ from the plot of $\ln P$ vs. $1/T$ (adsorption isosteres), since the slope is equal to $-\Delta H_{iso}/R$. The slope was determined using the polynomial fitting routine of degree 1, from which the isosteric heat was calculated. The results are shown in Fig. 4.58.

The isosteric heat plot show an initial sharp rise at very low coverage (i.e from 0.004 to 0.018 mmolg$^{-1}$), indicating that the surface of barium sulphate is homogeneous.

<table>
<thead>
<tr>
<th>AMOUNT ADSORBED mmolg$^{-1}$</th>
<th>CORRELATION COEFFICIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00448</td>
<td>0.8274</td>
</tr>
<tr>
<td>0.00568</td>
<td>0.8547</td>
</tr>
<tr>
<td>0.00652</td>
<td>0.8675</td>
</tr>
<tr>
<td>0.00737</td>
<td>0.8802</td>
</tr>
<tr>
<td>0.00837</td>
<td>0.8887</td>
</tr>
<tr>
<td>0.00946</td>
<td>0.9134</td>
</tr>
<tr>
<td>0.0100</td>
<td>0.9213</td>
</tr>
<tr>
<td>0.018</td>
<td>0.9245</td>
</tr>
<tr>
<td>0.0115</td>
<td>0.9314</td>
</tr>
<tr>
<td>AMOUNT ADSORBED (mmol g(^{-1}))</td>
<td>CORRELATION COEFFICIENT</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>0.0126</td>
<td>0.9295</td>
</tr>
<tr>
<td>0.0133</td>
<td>0.9232</td>
</tr>
<tr>
<td>0.0141</td>
<td>0.9253</td>
</tr>
<tr>
<td>0.0149</td>
<td>0.9293</td>
</tr>
<tr>
<td>0.0154</td>
<td>0.9269</td>
</tr>
<tr>
<td>0.0168</td>
<td>0.9359</td>
</tr>
<tr>
<td>0.0172</td>
<td>0.9401</td>
</tr>
<tr>
<td>0.0181</td>
<td>0.9411</td>
</tr>
<tr>
<td>0.0189</td>
<td>0.9543</td>
</tr>
<tr>
<td>0.0198</td>
<td>0.9505</td>
</tr>
<tr>
<td>0.0205</td>
<td>0.9445</td>
</tr>
<tr>
<td>0.0214</td>
<td>0.9438</td>
</tr>
<tr>
<td>0.0223</td>
<td>0.9507</td>
</tr>
<tr>
<td>0.0235</td>
<td>0.9355</td>
</tr>
<tr>
<td>0.0250</td>
<td>0.9310</td>
</tr>
<tr>
<td>0.0265</td>
<td>0.9523</td>
</tr>
<tr>
<td>0.0280</td>
<td>0.9566</td>
</tr>
<tr>
<td>0.0295</td>
<td>0.9490</td>
</tr>
<tr>
<td>0.0310</td>
<td>0.9480</td>
</tr>
<tr>
<td>0.0315</td>
<td>0.9423</td>
</tr>
<tr>
<td>0.0332</td>
<td>0.9355</td>
</tr>
<tr>
<td>0.0353</td>
<td>0.9408</td>
</tr>
<tr>
<td>0.0374</td>
<td>0.9568</td>
</tr>
<tr>
<td>0.0382</td>
<td>0.9738</td>
</tr>
<tr>
<td>0.0396</td>
<td>0.9816</td>
</tr>
<tr>
<td>0.0404</td>
<td>0.9880</td>
</tr>
</tbody>
</table>
From the correlation coefficients in Table 4.34 shows that at low coverages i.e less than 0.02 mmolg\(^{-1}\) has correlation coefficients of less than 0.94. This may be too large a difference to successfully use this approximate method of calculating \(H_{iso}\). This method of three temperatures or even simpler method of two temperatures has been widely used, but at high coverage. In this work we achieve very low coverages, and show that limitations are observed. Grillet et. al (1976) have compared the isotherm method with the calorimetric method to determine the isosteric heat of
Fig. 4.58 Isosteric heat plot of nitrogen on sample 1 at 80.1K (average)

\[ Vm(BET) = 0.0887 \text{ mmolg}^{-1} \]

Amount adsorbed (mmolg\(^{-1}\))
adsorption for N$_2$ on silicas (Gasil 35, Davidson 62 and Davidson 950) between 77K to 87K. These workers have showed that the isotherm method shows an initial steep rise up to a coverage of 0.5 whereas the calorimetric method showed a steep decrease in the isosteric heat within the same coverage range. However, above coverages of 0.5, both methods gave very similar results. Hence, using the isotherm method, only coverages above 0.5 should be used in the calculation of isosteric heat.

Furthermore, isotherms of krypton has generally been used for isosteric heat determinations. From the SED's we see that N$_2$ has far more specific interactions with the surface of barium sulphate and this may complicate isosteric heat determinations by this method.

The isosteric heat plot shows almost a plateau region between 0.015 and 0.035 mmol g$^{-1}$. This is followed by a steep rise to a maximum at 0.068 mmol g$^{-1}$, then an exponential decay at higher coverages. The subsequent rise is attributed to lateral interactions of the adsorbate. The BET $V_m$ occurs after the peak at approximately $1/3$ at the way along the exponential decay.

4.7.4. Heterogeneity Analysis

4.7.4.1. Smoothing

The smoothing parameters obtained from the HILDA method are presented in Table 4.36, 4.37 and 4.38, for the three isotherms. Again we see that SM2 and rms values are much lower for the Hill-de Boer model than the Langmuir model.
4.7.4.2. **Comparison of $V_m$**

The multilayer corrected $V_m$ were compared with the BET $V_m$ in the Table 4.35 below.

<table>
<thead>
<tr>
<th>TEMPERATURE/K</th>
<th>BET</th>
<th>$V_m$/mmolg$^{-1}$</th>
<th>MULTILAYER CORRECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.8</td>
<td>0.0887</td>
<td>0.0861</td>
<td></td>
</tr>
<tr>
<td>80.8</td>
<td>0.0551</td>
<td>0.0540</td>
<td></td>
</tr>
<tr>
<td>81.6</td>
<td>0.0503</td>
<td>0.0507</td>
<td></td>
</tr>
</tbody>
</table>

Both the BET model and multilayer correction monolayer volumes are in general in very good agreement for the temperatures studied. Differences are of the order of 0.03%.

4.7.5. **Energy Distributions**

4.7.5.1. **Hill-de Boer Model**

The HILDA method was used to determine the SED's for the nitrogen data at 77.8K, 80.8K and 81.6K. Fig. 4.59 shows the SED's for the Hill-de Boer model plotted on a scale suited to show the multilayer rise near 4.5 kJmol$^{-1}$. Details of the SED's features above 4.5 kJmol$^{-1}$ is shown in Fig. 4.60. The three SED's are similar but by no means identical.

The multilayer corrected SED are presented in Fig. 4.61. The 80.8K and 81.6K SED's are translated by nearly 0.8 kJmol$^{-1}$ to higher energy compared to the 77.8K SED. Three regions have been labelled,
<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>NUMBER OF DATA POINTS</th>
<th>MODEL</th>
<th>MULTILAYER CORRECTION</th>
<th>NUMBER OF ITERATIONS</th>
<th>r.m.s.</th>
<th>SM1</th>
<th>SM2</th>
<th>Vm/ mmol g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>153</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0317</td>
<td>0.0011</td>
<td>0.0168</td>
<td>0.2164</td>
</tr>
<tr>
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<td>153</td>
<td>HdB</td>
<td>NO</td>
<td>44</td>
<td>0.0107</td>
<td>0.0011</td>
<td>0.0055</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>144</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0091</td>
<td>0.0012</td>
<td>0.0094</td>
<td>0.0861</td>
</tr>
<tr>
<td>N₂</td>
<td>153</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3256</td>
<td>0.0011</td>
<td>0.1426</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>144</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.3019</td>
<td>0.0012</td>
<td>0.1445</td>
<td>0.0861</td>
</tr>
<tr>
<td>N₂</td>
<td>153 (RANDOMISED)</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0112</td>
<td>0.0012</td>
<td>0.0115</td>
<td>0.2164</td>
</tr>
<tr>
<td>N₂</td>
<td>153 (RANDOMISED)</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3037</td>
<td>0.0012</td>
<td>0.2249</td>
<td>0.2164</td>
</tr>
<tr>
<td>ADSORBATE</td>
<td>NUMBER OF DATA POINTS</td>
<td>MODEL</td>
<td>MULTILAYER CORRECTION</td>
<td>NUMBER OF ITERATIONS</td>
<td>r.m.s.</td>
<td>SM1</td>
<td>SM2</td>
<td>Vm/ mmolg⁻¹</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------</td>
<td>-------</td>
<td>-----------------------</td>
<td>----------------------</td>
<td>-------</td>
<td>------</td>
<td>------</td>
<td>-------------</td>
</tr>
<tr>
<td>N₂</td>
<td>101</td>
<td>HdB</td>
<td>NO</td>
<td>15</td>
<td>0.0134</td>
<td>0.0007</td>
<td>0.0057</td>
<td>0.1235</td>
</tr>
<tr>
<td>N₂</td>
<td>83</td>
<td>HdB</td>
<td>YES</td>
<td>15</td>
<td>0.0041</td>
<td>0.0006</td>
<td>0.0028</td>
<td>0.0540</td>
</tr>
<tr>
<td>N₂</td>
<td>101</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.1902</td>
<td>0.0007</td>
<td>0.0272</td>
<td>0.1235</td>
</tr>
<tr>
<td>N₂</td>
<td>83</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.1662</td>
<td>0.0006</td>
<td>0.0279</td>
<td>0.0540</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ADSORBATE</th>
<th>NUMBER OF DATA POINTS</th>
<th>MODEL</th>
<th>MULTILAYER CORRECTION</th>
<th>NUMBER OF ITERATIONS</th>
<th>r.m.s.</th>
<th>SM1</th>
<th>SM2</th>
<th>Vm/ mmolg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>100</td>
<td>HdB</td>
<td>NO</td>
<td>10</td>
<td>0.0554</td>
<td>0.0009</td>
<td>0.0096</td>
<td>0.1109</td>
</tr>
<tr>
<td>N₂</td>
<td>72</td>
<td>HdB</td>
<td>YES</td>
<td>11</td>
<td>0.0525</td>
<td>0.0010</td>
<td>0.0077</td>
<td>0.0507</td>
</tr>
<tr>
<td>N₂</td>
<td>100</td>
<td>LANGMUIR</td>
<td>NO</td>
<td>15</td>
<td>0.3673</td>
<td>0.0009</td>
<td>0.0531</td>
<td>0.1109</td>
</tr>
<tr>
<td>N₂</td>
<td>72</td>
<td>LANGMUIR</td>
<td>YES</td>
<td>15</td>
<td>0.3670</td>
<td>0.0010</td>
<td>0.0395</td>
<td>0.0507</td>
</tr>
</tbody>
</table>
Fig. 4.59 The site energy distribution functions obtained by HILDA from the Hill-de Boer analysis of the adsorption of nitrogen on sample 1 at 77.8, 80.8 and 81.6K.
Fig. 4.60  Detailed plot of the site energy distributions in Fig. 4.59 above 4.5kJmol⁻¹

At 77.8K  --- ---  At 80.8K  -----  At 81.6K
Fig. 4.61 The site energy distribution functions from Fig. 4.59 with the application of the multilayer correction.
region A, the high energy sites, region B, the intermediate energy sites and region C, the low energy sites. Region A for the three SEDs are similar allowing for some translation along the energy axis. Region B shows similar features for the 80.8K and 81.6K SED's but the 77.8K SED has similar features except the area under the features are smaller. Region C shows that the maximum for the low energy sites for each temperature is: for 77.8K is at approximately 5.5 kJmol$^{-1}$, for 80.8K is at 6.4 kJmol$^{-1}$ and for 81.6K is at approximately 6.9 kJmol$^{-1}$.

4.7.5.2. Langmuir Model

This nitrogen data was also analysed using the Langmuir model, the SED's are shown in Fig. 4.62, where the steep rise near 8.8 kJmol$^{-1}$ is due to multilayer formation. Details of features above 10 kJmol$^{-1}$ is shown in Fig. 4.63. The three SEDs show similar features except that the area under the 77.8K SED is smaller.

The multilayer corrected SED's are presented in Fig. 4.64. Again three regions are labelled in the same way as the Hill-de Boer SED's. Region A is similar for all three SED's except that the 77.8K begins at 18.1 kJmol$^{-1}$ while the 80.8K and 81.6K begin at 19.1 kJmol$^{-1}$. As with the Hill-de Boer results, the area of the 77.8K SED is smaller than the 80.8K and 81.6K SED's. Region C shows that the maximum peak for 77.8K is at 9.9 kJmol$^{-1}$, for 80.8K it is at 10.8 kJmol$^{-1}$ and for 81.6K it is at 11.25 kJmol$^{-1}$. 
The site energy distribution functions obtained by HILDA from the Langmuir analysis of the adsorption of nitrogen on sample 1 at 77.8, 80.8 and 81.6K.

At 77.8K

At 80.8K

At 81.6K

F(U) (molkJ⁻¹)

U (kJmol⁻¹)
Fig. 4.63 Detailed plot of the site energy distributions in Fig. 4.62 above 10kJmol⁻¹

At 77.8K

At 80.8K

At 81.6K
Fig. 4.64 The site energy distribution functions from Fig. 4.62 with the application of the multilayer correction

At 77.8K

At 80.8K

At 81.6K
4.7.5.3. Further Considerations

Both the Hill-de Boer and Langmuir model SED's show large differences at low energy in peak heights and positions, and because of the normalisation of the total area under the three SED's to 1, differences here will be reflected elsewhere. However, the differences in area of the peaks at low energy do not appear to be substantial.

The key feature at high energy that we propose as the best monitor of surface modifications for barium sulphate shows good qualitative agreement at the three temperatures; the same predominantly bimodal feature is clearly reproduced. The agreement is particularly good between the SED's at the two higher temperatures at high energy, and agreement at these temperatures is shown throughout the energy range, although to a lesser extent.

In region B, the 77.8K SED is well below the others and we suggest that this is strongly linked to the large peak near the monolayer. Further investigation of termination of the SED would be profitable. For example, termination of the 77.8K SED at 5 kJmol$^{-1}$ would bring it closer to the other two and in that case, the area under the peak centred close to 4.6 kJmol$^{-1}$ would add to the remainder of the energy distribution.

Another way of describing the differences in the results in Figs. 4.60-4.64 is the observation that translation of the lower temperature energy distribution along the energy axis by approximately 0.8 kJmol$^{-1}$ would yield closer agreement.
CHAPTER 5

CONCLUSIONS
Conclusions

The main objective of this investigation was to study the sensitivity of the heterogeneity analysis in the detection of various amounts of preadsorbed material on the surface of barium sulphate. This is the first investigation of this kind, utilising the heterogeneity analysis for these type of samples. An additional question posed was whether this method of heterogeneity analysis would give further insight governing the type of surface sites affected by the adsorption of STPP on the surface of barium sulphate.

5.1. Heterogeneity Analysis

5.1.1. Smoothing of Data

The smoothing is necessary to prevent non-existent structure from being introduced into the solution of the energy distribution function in the integral equation from the experimental error in the measured isotherms. While significant smoothing is needed, too much smoothing obviously can destroy information in the original data. The smoothing procedure adopted in this work (Chapter 2) has been chosen to give some degree of over-smoothing because there is sufficient information given in this case for analysis while producing highly reliable energy distributions for the adsorbate-adsorbent system studied in this work.

5.1.2. Models

Another factor which has the potential of affecting the solution of the energy distribution is the choice of local isotherm function in the integral equation. This factor has been examined in this
study, which indicates that using different, though still reasonable, local isotherm functions results are best found for the Hill-de Boer and Fowler-Guggenheim model compared with the Langmuir model. Although the energy distributions for the three models are qualitatively similar.

Since, the Hill-de Boer and Fowler-Guggenheim models gave virtually identical energy distributions, hence the Hill-de Boer and Langmuir models appear throughout this study.

The Hill-de Boer energy distributions were found to be continuous, whereas, for the Langmuir model, the energy distribution was discontinuous i.e including regions where f(U) = 0. Also, the Langmuir model energy distributions are 'expanded' on the vertical scale compared to the Hill-de Boer energy distributions. House et. al (1978, 1982) has shown that the Langmuir and Hill-de Boer models give similar energy distributions from the HILDA method. As with this work, they found that the major differences between the two models for all the systems studied is the height of the peaks.

From the rms and SM2 values indicate that the Hill-de Boer model showed less deviations between the final computed isotherm and experimental data. This suggests that the mobile model of adsorption are capable of producing significantly better agreement between the computed and experimental isotherm. However, the essential features and shape of the energy distributions are independent of the local isotherm function used. These findings are in agreement with House et. al (1982).

Furthermore, the virial equation used in the CAEDMON method gives very similar results to that obtained by the Hill-de Boer model, using the HILDA method.
5.1.3. **Stability of SED's**

The stability of the energy distributions determined from the HILDA method was investigated in two ways:

1. By increasing the number of iterations with the HILDA method
2. By randomising the experimental isotherm with a specified standard deviation of ± 1%.

Both these methods showed that the energy distributions obtained in this work were very stable. From (i), the results showed that a minimum number of 15 iterations are required to obtain good agreement between the computed isotherm with that of the experimental isotherm. Other workers (House et. al (1984), Leng and Clark (1982) and Hope (1985) have showed for the systems N₂/silica, Kr/aerosils and Kr/silicates, respectively that the stability of the energy distributions is remarkably good with the HILDA method.

5.1.4. **Termination at the Monolayer**

Estimates of the monolayer value for the termination of the SED include:

(i) Before the steep rise at low energy in the energy distribution due to the formation of multilayers.

(ii) The BET monolayer volume.

(iii) The multilayer correction monolayer volume.

House (1975) and House and Jaycock (1978) compared (i) and (ii) and showed that the monolayer volumes are similar for the two methods, although HILDA gave slightly larger values. Recently, House et. al (1981, 1984) has used the multilayer correction method for the termination at the monolayer volume, since both the BET and
The multilayer correction method gives similar monolayer volume, and the latter is easy to use. All the isotherm data that covered the multilayer region in this work was corrected using the multilayer correction. In addition, the full range energy distribution are presented. The application of the multilayer correction to the fuller ranging data amplifies the submonolayer features of the energy distribution because both SED's are normalised to unit areas.

Discrepancies just below the monolayer were found for both the Hill-de Boer and Langmuir model energy distribution, although below the monolayer, the energy distributions show qualitatively very similar features. The Hill-de Boer model energy distributions showed slightly less discrepancies than the Langmuir model when compared to the respective full range energy distribution.

As with the HILDA method, the CAEDMON method energy distributions showed discrepancies just below the monolayer, depending on the method of termination i.e BET or multilayer correction method.

Further investigations are necessary to the method chosen for the termination of the data at the monolayer in the heterogeneity analysis. To be consistent in this work, the multilayer correction was applied to the isotherm data for each system investigated in the multilayer region.

5.2. Normalization Procedure

A normalisation procedure was employed for the first time in the heterogeneity analysis. This normalisation procedure was applied to isotherm data terminating at low pressures, well below the monolayer (in this work up to 1 mmHg), and various system could be compared in a similar manner had the full range data was available.
This normalisation procedure was first examined with a known full complement of data i.e the data of nitrogen on barium sulphate with various amounts of preadsorbed STPP at 77.8K. The energy distribution obtained from the normalisation procedure for the limited data (up to 1 mmHg) and that of the full data showed that the features were very similar i.e the relative peak heights and areas were found to be in good agreement. Having ascertained that the normalisation procedure gives reasonable results, it was utilised for the following low pressure data obtained in this study:

(i) Carbon monoxide on sample 1 and 2 at 77.8K
(ii) Nitrogen on sample 1 and 4 at 77.8K.

The results of the heterogeneity analysis for (i) and (ii) will be discussed later.

5.3. Characterization of barium sulphate (Sample 1): Energy Distributions

5.3.1. \( \text{N}_2, \text{CO}, \text{Ar} \) and \( \text{Kr} \) as Adsorbates

Barium sulphate was characterised by argon, krypton, nitrogen and carbon monoxide. The argon and krypton atoms are non-polar whereas nitrogen and carbon monoxide possess quadrupole moments of 0.27 \( \text{A}^2 \) and 0.34 \( \text{A}^2 \) (Drain (1953)) respectively. Only carbon monoxide possesses a dipole moment of 0.12 Debye (Hirschfelder et. al (1953)). This is the first study where barium sulphate surface has been investigated using the heterogeneity analysis with four different adsorbates. All the energy distributions determined for the four adsorbates indicate that the surface of barium sulphate is heterogeneous.
The nitrogen and carbon monoxide energy distributions show two main features, one at high energy and the other at low energy, but are quantitatively different. Alignment of these two energy distributions at these respective monolayers show that carbon monoxide has a much stronger interaction with high energy sites, whereas nitrogen has a stronger interaction with the lower energy sites on the surface of barium sulphate. This may be due to the large dipole moment and quadrupole moment of the carbon monoxide molecule interacting very strongly with the ionic surface of barium sulphate.

Argon and krypton energy distributions do not show strong interactions with the high energy sites on the surface of barium sulphate as both are non-polar. However, for the low energy sites argon atoms show a stronger interaction compared to krypton atoms.

Comparing the energy distributions of argon and nitrogen aligned at the monolayer shows that both adsorbates have a strong interaction with low energy sites on the barium sulphate surface. Hinman and Halsey (1977) have shown similar results with nitrogen and argon on rutile using the CAEDMON method. Also Drain and Morrison (1953) obtained energy distributions from calorimetric results of oxygen and nitrogen which showed that both nitrogen and oxygen molecules interacted with the low energy sites on the surface of rutile (TiO$_2$). However, the nitrogen energy distribution for rutile showed some interaction with the high energy sites, but no distinct feature as with that obtained for barium sulphate sample.

Alignment of the argon and krypton energy distributions at the monolayer shows that krypton interacts weakly with the low energy
sites compared to argon, but interacts strongly with the mid-range energy sites. The full range energy distribution (i.e. without the application of the multilayer correction) shows virtually an exponential decay with increasing energy, but distinct peaks may be observed. Similar energy distributions have been obtained for argon on maximally hydroxylated silica (House (1978)), krypton on Gasil I or Aerosil (Leng and Clarke (1982)).

House and Jaycock (1977) related the single peak from the krypton and argon energy distributions obtained from the HILDA method for sodium chloride to the (100) plane. After annealing the sample showed that the peak height was reduced. No such inference can be made from the energy distributions obtained for barium sulphate because of the far more complex ED due to the large number of crystal planes available during growth.

5.4. Temperature Variation and Isosteric Heat

Temperature dependent results provide further information on the heterogeneity analysis but raise further questions and consideration of the approximations used. The calculation of the isosteric heat from adsorption isotherms rather than from calorimetric measurements involves approximations and this work highlights difficulties at very low coverages. This result is in agreement with the work of Grillet et al (1976), where limitations were seen at coverages below 0.5, but nevertheless were far higher than the values reached in this work.

While the amount of gas adsorbed on a surface is temperature dependent, the distribution of surface sites is not so that
differences observed must be ascribed to experimental errors and errors from the approximations used in the analysis. The use of energy distribution in monitoring surface changes should clearly be done at fixed temperature and of course this is the most practical approach, and errors from the temperature dependent effects of heterogeneity analysis techniques do not interfere with the investigation of physical changes to a sample surface.

In terms of developing the heterogeneity analysis technique, however, information on the temperature dependence is very important and worth the effort involved. We present the results of this part of the work as subject matter for further interpretation.

The isosteric heat curve shows a maxima at coverages approaching the monolayer, while the BET monolayer is observed a third of the way along the rapid drop. Beebe et. al (1954) and Steele (1974) have suggested that the monolayer on a homogeneous surface is complete at a coverage that corresponds to the mid-point of the rapid drop in the isosteric heat curve. The most homogeneous surface that has been extensively studied is that of graphitised carbon blacks. Well defined maxima in the isosteric heat curves have been reported for many gases (Sing (1973), Augul and Kiselev (1970)) to lateral adsorbate-adsorbate interactions giving first attraction and then repulsion as coverages approach the monolayer.

5.5. Comparison of barium sulphate samples

5.5.1. \( \text{N}_2 \)

Barium sulphate prepared by the author (sample 1) was compared with barium sulphate prepared at Unilever Research, Port Sunlight Laboratories (sample 4) using the heterogeneity analysis. The normalisation procedure was employed for the nitrogen data.
The general characteristics of the energy distributions obtained from the Hill-de Boer model using the HILDA method were very similar. The peak positions and heights were similar for both samples suggesting that this portion of the energy distribution is like a "fingerprint" region. However, the general features within the Langmuir model energy distributions are similar for sample 1 and 4, but indicates that sample 4 has more high energy sites compared to sample 1.

5.5.2. \textit{Kr}

The krypton energy distributions for sample 1 and 4 show the same number and positions of the peaks over a broad mid-energy range. However, the general shape of the Hill-de Boer energy distribution is "bell" shaped for sample 4 whereas, sample 1 is "rectangular" shaped.

Silica samples have been well characterised using this heterogeneity analysis by several workers (House, (1978); Leng and Clark (1982); and Van Dongen (1973)) using argon by the former workers and the latter two workers used krypton, all showing a exponential decay in the energy distribution with increasing energy. These results suggest that sample surfaces may be characterised using a specific adsorbate using the heterogeneity analysis. However, further use of the heterogeneity analysis must be completed for many different solid surfaces before the above statement can be fully justified.
5.6. Pre-adsorbed STPP onto barium sulphate

5.6.1. $\text{N}_2$

This is the first study where the HILDA and CAEDMON methods have been employed to investigate the heterogeneity of surfaces of barium sulphate with preadsorbed material i.e STPP. Nitrogen and carbon monoxide gases were used, as they both showed specific features within the energy distributions for barium sulphate surface that may be sensitive to the various amounts of STPP present.

The HILDA method results for the mobile and localised models clearly show that a majority of high energy sites are lost by covering the barium sulphate surface with 38% monolayer coverage of STPP from the nitrogen data. Further coverage of up to monolayer STPP shows a further reduction in the high energy sites may also be seen. However, with loss of high energy sites, further low energy sites are generated with increasing coverage of STPP on the barium sulphate surface.

If the nitrogen energy distributions are divided into two regions denoted high energy sites and the low energy sites, then from the areas of these sites indicate that virtually all the high energy sites are lost with a 38% monolayer coverage of STPP. While the area of the monolayer coverage shows very little difference to the 38% monolayer coverage. This would suggest that only a small amount of STPP would be required to eliminate the high energy sites on the surface of barium sulphate.
5.6.2. **CO**

Carbon monoxide gas was used to probe the surfaces of barium sulphate (sample 1) and barium sulphate with 38% monolayer coverage of STPP (sample 2) at low pressure, hence the normalisation procedure was used in the heterogeneity analysis. The Hill-de Boer model energy distributions from the HILDA method showed a distinct bimodal peak at high energy for sample 1, however, with sample 2 the higher energy site of this bimodal peak is vastly reduced. This would indicate the carbon monoxide may be more specific than nitrogen in studying these modifications.

5.6.3. **CAEDMON Method**

The nitrogen data for the preadsorbed samples were analysed using the CAEDMON method. The results from the CAEDMON method and the Hill-de Boer model from the HILDA method are remarkably similar. This result is in accordance with comparison of HILDA and CAEDMON (House and Jaycock (1977)) using data for the adsorption on silver iodide and nitrogen on Spheron 6, but the HILDA method showing additional detail. Recently, House et. al.(1982) have shown reasonable agreement for the two methods for the data of nitrogen on chemically modified silicas.

From this study, we conclude that both the HILDA and CAEDMON methods are sensitive to the preadsorption of STPP onto the surface of barium sulphate. It is satisfying that these two approaches give this agreement.
5.7. Inhibitors

As poly-phosphates are well known inhibitors of precipitates such as strontium sulphate (Miura et al., 1966; Miura et al., 1962); Naona (1967) and Otani (1960) and barium sulphate (Leung and Nancollas, 1978, 1978a); Nancollas and Liu (1975); Rizkalla (1983) and Smith (1983), and the inhibition has been attributed to the loss of surface growth sites (Nancollas, 1968) and that only a small amount of additives are required on the surface of the precipitate (Leung and Nancolas, 1978, 1978a) to inhibit crystal growth.

The results from the heterogeneity analysis strongly support the findings of Leung and Nancollas (1978, 1978a) that specific sites on the surface of barium sulphate are vastly affected by the presence of STPP in small amounts. The results indicate further that specific high energy sites may be involved in the retardation of barium sulphate precipitate.

It is concluded in this work that the heterogeneity analysis is a strong and powerful technique for characterising surface phenomena.

5.8. Further Work

It would be interesting to investigate the degree of sensitivity of the Heterogeneity Analysis technique by studying samples with lower levels of coverage e.g. 5% STPP on the surface of barium sulphate using nitrogen and carbon monoxide as the gas probes. The latter probe may give further information regarding the specific high energy sites involved in the retardation of crystal growth of barium sulphate with STPP. Other inhibitors may also be studied on different adsorbents which may give further information or support on the mechanisms of inhibition of crystal growth.
Further investigations are necessary to define rigorous termination of the data at the monolayer, however, consistent procedures are available at present.

The temperature dependence of the energy distributions is a major subject involving experimental and theoretical aspects of Heterogeneity analysis.

The experimental adsorption isotherms determined in this investigation are very accurate and detailed, hence these may be further analysed to study:

i) the predictability of monolayer and multilayer models to that of the experimental data

ii) to estimate the specific surface area with various multilayer models

iii) the surface heterogeneity using different methods to calculate the site energy distributions.
Appendix I shows the smoothed data (represented by a continuous line) to the original experimental data (represented by individual points) of the adsorption isotherm by using a graphic routine called MULTPLOT. The following data are presented:

Figs.A.1.a-d Adsorption isotherm of nitrogen at 77.8K on sample 4.
Figs.A.2.a-f Adsorption isotherm of nitrogen at 77.8K on sample 1.
Figs.A.3.a-e Adsorption isotherm of nitrogen at 80.8K on sample 1.
Figs.A.4.a-e Adsorption isotherm of nitrogen at 81.6K on sample 1.
Figs.A.5.a-e Adsorption isotherm of nitrogen at 77.8K on sample 2.
Figs.A.6.a-e Adsorption isotherm of nitrogen at 77.8K on sample 3.
Figs.A.7.a-d Adsorption isotherm of krypton at 77.8K on sample 4.
Figs.A.8.a-d Adsorption isotherm of krypton at 77.8K on sample 1.
Figs.A.9.a-e Adsorption isotherm of argon at 77.8K on sample 1.
Figs.A.10.a-e Adsorption isotherm of carbon monoxide at 77.8K on sample 1.
Figs.A.11.a-d Adsorption isotherm of carbon monoxide at 77.8K on sample 2.
Fig. A.1.1.a Adsorption isotherm of nitrogen at 77.8K on sample 4
Fig. A1.1b Adsorption isotherm of nitrogen at 77.8K on sample 4
Fig. A.1.1.c Adsorption isotherm of nitrogen at 77.8K on sample 4
Fig. A.1.1.d Adsorption isotherm of nitrogen at 77.8K on sample 4

Amount adsorbed (mmolg⁻¹)

Equilibrium pressure (kPa)

0.03 0.06 0.09
Fig. A.1.2.a Adsorption isotherm of nitrogen at 77.8K on sample 1
Fig. A.1.2.b Adsorption isotherm of nitrogen at 77.8K on sample 1
Fig. A.1.2.c Adsorption isotherm of nitrogen at 77.8K on sample 1
Fig. A.1.2.d Adsorption isotherm of nitrogen at 77.8K on sample 1

![Graph showing adsorption isotherm of nitrogen at 77.8K on sample 1. The x-axis represents equilibrium pressure (kPa), ranging from 0.02 to 0.08, and the y-axis represents amount adsorbed (mmol g⁻¹). The data points are connected by a line, showing a curve that increases as the equilibrium pressure increases.]
Fig. A.1.2.e  Adsorption isotherm of nitrogen at 77.8K on sample 1

Equilibrium pressure (kPa)
Fig. A.1.2.f  Adsorption isotherm of nitrogen at 77.8K on sample 1

Equilibrium pressure (kPa)

Amount adsorbed (mmol g⁻¹)
Fig. A.1.3.a Adsorption isotherm of nitrogen at 80.8K on sample 1

Equilibrium pressure (kPa)

Amount adsorbed (mmolg$^{-1}$)
Fig. A.1.3.5 Adsorption isotherm of nitrogen at 80.8K on sample 1
Fig. A.1.3.c Adsorption isotherm of nitrogen at 80.8K on sample 1

Amount adsorbed (mmolg⁻¹) vs Equilibrium pressure (kPa)
Fig. A.1.3.d  Adsorption isotherm of nitrogen at 80.8K on sample 1
Fig. A.1.3.è Adsorption isotherm of nitrogen at 80.8K on sample 1.
Fig. A.1.4.a Adsorption isotherm of nitrogen at 81.6K on sample 1
Fig. A.1.4.b Adsorption isotherm of nitrogen at 81.6K on sample 1.
Fig. A.1.4.c  Adsorption isotherm of nitrogen at 81.6K on sample 1.
Fig. A.1.4.d Adsorption isotherm of nitrogen at 81.6K on sample 1

Amount adsorbed (mmol g$^{-1}$)

Equilibrium pressure (kPa)
Fig. A.1.4.e  Adsorption isotherm of nitrogen at 81.6K on sample 1
Fig. A.1.5.a Adsorption isotherm of nitrogen at 77.8K on sample 2
Fig. A.1.5.b Adsorption isotherm of nitrogen at 77.8K on sample 2
Fig. A.1.5.c Adsorption isotherm of nitrogen at 77.8K on sample 2
Fig. A.1.5.d Adsorption isotherm of nitrogen at 77.8K on sample 2
Fig. A.1.5.e  Adsorption isotherm of nitrogen at 77.8K on sample 2
Fig. A.1.6.a Adsorption isotherm of nitrogen at 77.8K on sample 3

Equilibrium pressure (kPa)

Amount adsorbed (mmolg⁻¹)
Fig. A.1.6.b Adsorption isotherm of nitrogen at 77.8K on sample 3

Amount adsorbed (mmol g⁻¹)

Equilibrium pressure (kPa)
Fig. A.1.6.c  Adsorption isotherm of nitrogen at 77.8K' on sample 3

Amount adsorbed (mmol-g⁻¹)

Equilibrium pressure (kPa)

0.002 0.004 0.006 0.008
Fig. A.1.6.d  Adsorption isotherm of nitrogen at 77.8K on sample 3

[Graph showing adsorption isotherm with x-axis labeled 'Equilibrium pressure (kPa)' and y-axis labeled 'Amount adsorbed (mmolg⁻¹)']
Fig. A.1.6.e Adsorption isotherm of nitrogen at 77.8K on sample 3

Equilibrium pressure (kPa)

Amount adsorbed (mmol/g)
Fig. A.1.7.a Adsorption isotherm of krypton at 77.8K on sample 4
Fig. A.1.7.b  Adsorption isotherm of krypton at 77.8K on sample 4
Fig. A.1.7.c Adsorption isotherm of krypton at 77.8K on sample 4
Fig. A.1.7.d Adsorption isotherm of krypton at 77.8K on sample 4
Fig. A.1.8.a Adsorption isotherm of krypton at 77.8K on sample 1
Fig. A.1.8.b Adsorption isotherm of krypton at 77.8K on sample 1
Fig. A.1.8.c Adsorption isotherm of krypton at 77.8K on sample 1
Fig. A.1.8.d  Adsorption isotherm of krypton at 77.8K on sample 1.
Fig. A.1.9.a Adsorption isotherm of argon at 77.8K on sample 1
Fig. A.2.9.b Adsorption isotherm of argon at 77.8K on sample 1
Fig. A.1.9.c Adsorption isotherm of argon at 77.8K on sample 1
Fig. A.1.9.d  Adsorption isotherm of argon at 77.8K on sample 1
Fig. A.1.9.e Adsorption isotherm of argon at 77.8K on sample 1

Equilibrium pressure (kPa)

Amount adsorbed (mmolg⁻¹)
Fig. A.1.10.a Adsorption isotherm of carbon monoxide at 77.8K on sample 1
Fig. A.1.10b  Adsorption isotherm of carbon monoxide at 77.8K on sample 1
Fig. A.1.10c Adsorption isotherm of carbon monoxide at 77.8K on sample 1
Fig. A.1.10.d  Adsorption isotherm of carbon monoxide at 77.8K on sample 1
Fig. A.1.10.e  Adsorption isotherm of carbon monoxide at 77.8K on sample 1
Fig. A.1.11a Adsorption isotherm of carbon monoxide at 77.8K on sample 2

Equilibrium pressure (kPa)

Amount adsorbed (mmol g⁻¹)
Fig. A.1.11.b Adsorption isotherm of carbon monoxide at 77.8K on sample 2
Fig. A.1.11.c Adsorption isotherm of carbon monoxide at 77.8K on sample 2

Equilibrium pressure (kPa)
Fig. A.1.11.d Adsorption isotherm of carbon monoxide at 77.8K on sample 2


