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## ABSTRACT

This is the first attempt to measure the relative distribution of energies on the surface of $BaSO_4$. Three samples were studied. Two of the samples were investigated after undergoing the same heat treatment, and the relative distribution of surface energy for both was found to be very similar. A third sample, tested after a prolonged heat treatment, was found to be more homogeneous and the distribution obtained more uniform. For all the samples approximately 60% of the surface was heterogeneous. For the two similar samples approximately 10% of the surface had energies from 3 to 4-1/2 times greater than the average $[\bar{\epsilon}_S(0)]$. Therefore, strong attraction for the two samples and some second phase was primarily due to 45% of the surface; whereas, for the third sample it was found to be 30%.

The observed heterogeneity is attributed to the presence of surface cavities which contribute not only to the excess energy on the surface, but to its surface area also. Their contribution to both was rendered inoperative by the preadsorption of the fatty acid. From this study we have concluded that dispersion forces are predominant on the

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surface of $BaSO_4$; this is reasonable for a molecular crystal such as $BaSO_4$.

# I. INTRODUCTION

In a recent publication[1] the theoretical description of the relative distribution of energy on a solid surface was derived and applied to the $TiO_2$ surface. Very little has been published on the surface properties of $BaSO_4$, and the nature of its heterogeneity is unknown. For this reason a detailed adsorption study of the $BaSO_4$-$N_2$ system, the effect of a preadsorbed fatty acid on its adsorption characteristics and on its energy distribution was undertaken in order to improve our understanding of its surface properties. This is the first attempt to obtain the relative distribution of energy on $BaSO_4$.

## II. EXPERIMENTAL

The type of apparatus used and preparation of the bare $BaSO_4$ samples prior to the adsorption measurements and its coating with stearic acid was exactly the same as that of the $TiO_2$ study.[2] Three samples of $BaSO_4$ were investigated. Two of the samples (designated as S1 and S2) were subjected to the same heat treatment (600°C for 6 days) and the third (sample B) received a prolonged heat treatment (600°C for 12 days) prior to the initial measurement. The samples were Baker's Analytical reagent grade and assayed 97% in purity. The greatest percentage of impurity was reported to be water soluble salts. In addition, $BaSO_4$ is known to contain water coprecipitated with $BaSO_4$ molecules and held in pockets in the crystallites;[3] Three molecules of water substitute for each $BaSO_4$ ion pair in the crystal lattice.* Wu and Copeland[4] have shown that this water cannot be completely removed at any temperature below 600°C and $10^{-6}$ mm Hg pressure. They fail to point out, however, that at these temperatures $BaSO_4$ has a tendency to agglomerate; this changes the surface area and, therefore, the adsorption capacity of the surface. If a sample is heated to these high temperatures (500° - 600°C) after each measurement in an effort to reproduce the isotherm, each degassing will allow for further agglomeration, a decrease in surface area; and perhaps further removal of any residual trapped water making reproducibility impossible. However, the surface preparation used in this study was such that the adsorption data were found to be completely reproducible.

* One barium sulfate group occupies about 86Å$^3$ (one-quarter of the unit cell) and three water molecules about 90Å$^3$.

## III. RESULTS AND DISCUSSION

### A. Adsorption Isotherms

The effect of preadsorbed stearic acid on the nitrogen adsorption isotherm of $BaSO_4$ is similar to that of $TiO_2$. Typical isotherms for bare and coated conditions at 77.5°K are shown in Fig. 1, where $\theta_\perp$ is the fraction of surface covered with preadsorbate calculated by assuming the perpendicular orientation; and $\theta_\parallel$ for the preadsorbate in the parallel orientation. The vertical line is the estimated error on the volume adsorbed.

Every experimental precaution was taken to guarantee that the reduction in the isotherm after the addition of the preadsorbate is due to masking by the long chain fatty acid. Evidence that the change in temperature during the measurement for each coating and the thermal pretreatment of the sample were not responsible for the reduced isotherm is seen in Table 1. where the temperature coefficients of the coated and uncoated sample (S1) are compared. These data were taken from the adsorption isotherm at 77.5°K and 90.2°K. The fact that the temperature coefficients are the same within experimental error for each coverage is convincing evidence that the samples are at the same temperature and that the kinetics are the same for both the coated and uncoated samples. Since the conditions of each measurement after coating are the same, and the sequence of heating and coating prior to the measurement has been standardized[2] any reduction in adsorption must be due to the coating of the surface. This also means that a comparison of the isosteric heats of adsorption for the bare and coated samples is justified since equilibrium conditions prevail.

Table 1. Temperature coefficients of sample S1.

| P(cm Hg) | $\theta_{\perp}$ | $\theta_{\parallel}$ | $\left(\frac{\Delta V}{\Delta T}\right) \times 100$ |
|---|---|---|---|
| 2 | 0 | 0 | 3.6% |
| 2 | 5% | 27% | 3.3% |
| 2 | 10% | 60% | 3.1% |
| 4 | 0 | 0 | 4.3% |
| 4 | 5% | 27% | 4.1% |
| 4 | 10% | 60% | 4.1% |
| 8 | 0 | 0 | 5.3% |
| 8 | 5% | 27% | 5.1% |
| 8 | 10% | 60% | 5.4% |
| 12 | 0 | 0 | 6.3% |
| 12 | 5% | 27% | 5.6% |
| 12 | 10% | 60% | 6.0% |

B. The Effect of Preadsorption on Surface Area Measurements

When the isotherms of Fig. 1 are plotted using the linear form of the B.E.T. equation, good straight lines are obtained in the range $P_i'/P_o$ = .05 to .35 as shown in Fig. 2. $P_i'$ is the equilibrium pressure and $P_o$ is the vapor pressure of the adsorbate at the temperature of experiment. As mentioned, $BaSO_4$ contains coprecipitated water present in pockets in the crystallites. The removal of this water from the pockets leaves cavities in the crystal and leads to the formation of a stable "substraction" lattice.[3] The effect of this removal on the surface is not certain, but it has been suggested by Wu and Copeland[4] that the surface may contain a proportionate share of these pockets. They had difficulty in reproducing their surface area results with $H_2O$ adsorption measurements and explained this nonreproducibility by the presence of surface cavities. If their explanation is correct, the preadsorption of a long-chain fatty acid which would tend to fill any cavities on the surface should result in a decrease of surface area for barium sulfate.

That this is actually the case is shown in Fig. 3. This decrease of surface area with preadsorbate verifies the suggestion of Wu and Copeland.[4] Both sample S1 and S2 are from the same bottle. The change in surface area for the former is 15% and for the latter 12%. After $\theta_{\|}$ = 27% there is no significant change in surface area for these two samples.

Sample B was from a new bottle. Its change in surface ares is 25%, and there is a change in its surface area up to $\theta_{\|}$ = 48%. It is rather interesting that it reaches essentially the same constant value of surface area as sample S1 (Fig. 3). Furthermore, the ratio of the fraction of the

respective surfaces covered when the surface areas become constant and the ratio of their change is the same for sample S1 and sample B--that is, two. Sample B was the last sample measured and was heated for a much longer time than the previous two. This may be the reason for any differences. For all three samples the fraction of the surface covered is approximately two times greater than the surface area change. The lowest accurate coverage possible was $\theta_{||}$ = 13%, which is exactly equal to the corresponding surface area change (13%) for sample B. This shows experimentally that at low coverage the preadsorbate will cover the highest energy sites which are, of course, the cavities due to the removal of water. Configurational effects are not important, and the long chain is more efficient in its coating. At the larger fractions of coverage, configurational effects are more important since the heat of adsorption on the less active cracks and smaller cavities is lower. It will take more molecules to cover these smaller defects since the adsorbed molecules come in contact with less ions as compared to the larger cavities.

It should be stated that the surface areas and the change that results from the preadsorption have been calculated by the form of the B.E.T. equation which is only valid for a non-porous adsorbent. $BaSO_4$ is a non-porous powder. Therefore, the change in surface area for the barium sulfate powders is attributed not to the porosity of the powder, but to the presence of surface cavities. Since these cavities have an average area of 22.29$Å^2$ and the area of a nitrogen molecule is 16.2$Å^2$, they will be occupies by nitrogen molecules initially and increase the amount adsorbed at any given pressure up to the pressure corresponding to monolayer coverage ($V_m$). After coating, these cavities are no longer available to

the nitrogen molecules, and $V_m$ will decrease. Adsorption and desorption of the nitrogen molecules from these cavities involve similar forces; there is no capillary condensation which results in hysteresis.

### C. Isosteric Heats of Adsorption for the $BaSO_4$-$N_2$ System

A typical plot of the isosteric heat of adsorption for the $BaSO_4$-$N_2$ system is shown in Fig. 4. The heat of adsorption is reported for both the perpendicular and parallel orientations. The shape of the differential heat curve is not uncommon.[5,6] The rise with the adsorbed gas coverage is attributed to the lateral van der Waal's forces between the adsorbed molecules. A maximum is reached, and then the heat decreased to the heat of condensation for nitrogen.

The total or integral experimental heats calculated up to a monolayer ($\Delta H_m$) for nitrogen on the three $BaSO_4$ samples are tabulated in Table 2 as a function of the fraction of surface covered with the preadsorbate along with the heats calculated from the constant C of the B.E.T. equation. The fact that the net heats as calculated from the B.E.T. parameter C are smaller than the measured is a good indication that the measured heats are reasonable. Brunauer[7] mentions that the B.E.T. heats can be even smaller than 50% of the measured value. This is considered an upper limit. Much higher heat values than the ones reported in Table 2 could only be obtained if the heat curves started at a very high value and progressively decreased as the amount adsorbed increases. As pointed out, this shape was obtained for the $TiO_2$-$N_2$ system,[2] and the explanation for this type of curve is that the first molecules to arrive at the surface are preferentially adsorbed at high energy sites giving off large quantities of heat; as more molecules arrive, these sites become filled and only the less active sites

Table 2

The measured isosteric heat integrated up to the monolayer coverage ($\Delta H_m$) and the net heat as calculated from the C constant of the B.E.T. equation for the $BaSO_4$ samples.

| | Sample | $\theta_{\parallel}$ (%) | $\theta$ (%) | $\Delta H_m (\frac{ergs}{cm^2})$ Experimental total | $\Delta H_m (\frac{ergs}{cm^2})$ B. E. T. |
|---|---|---|---|---|---|
| | S2 | 0 | 0 | 123.02 | 82.42 |
| A | B | 0 | 0 | 98.41 | 88.820 |
| | S1 | 0 | 0 | 112.140 | 88.820 |
| | S2 | 27.49 | 5 | 86.58 | 75.69 |
| B | B | 13.21 | 2.34 | 88.02 | 82.07 |
| | S1 | 26.98 | 5 | 83.26 | 77.34 |
| | S2 | | | | |
| C | B | 48.00 | 8.57 | 84.500 | 79.66 |
| | S1 | 60.19 | 10 | 76.01 | 76.16 |
| | S2 | 112.35 | 20 | 75.23 | 73.92 |
| D | B | 65.75 | 11.78 | 80.20 | 79.66 |
| | S1 | 116.61 | 20 | 69.46 | 76.16 |

are available. This type of curve is not impossible for the $BaSO_4$-$N_2$ system, but is unlikely for the surface preparation used and for the magnitude of heat which would result. Heats which are from four to five times the heats calculated from the B.E.T. equation are the exception.

Sample B received a different heat treatment than sample S1 or sample S2. It was also from a different reagent bottle. Nevertheless, the heat of adsorption for the uncoated samples are of the same order of magnitude (Column 4, Table 2), which indicates that the same forces are operative from sample to sample. Sample B was measured in an effort to study the effect of a different surface preparation and to see if a sample from a different reagent bottle would be significantly different from the other two samples. It received a much longer heat treatment (two weeks at 600°) than the other two and, therefore, should be more homogeneous. The experimental heat of adsorption is lower for sample B, and its change in the heat of adsorption with preadsorbate coverage is also small compared to the other samples. There are many plausible and consistent explanations for these differences; however, none of them can be proven with certainty. The reason for this is the experimental results are average quantities which reflect an underlying microscopic interaction but does not real its precise nature. In addition, the shape, orientation, true size, etc., of the cavities on the surface of $BaSO_4$ and hence on the numerous possible planes ({100} , {110} , etc.) which make up the surface of the powder is not known. Nevertheless, one possible explanation for the lower heats of adsorption for sample B is that a long heat treatment results in a tendency to form cavity pairs on the surface and, hence, reduce the surface area.

The cavities are larger and can accomodate more nitrogen atoms. This facilitates the possibility of interaction between the adsorbed atoms which can be larger than that due to the interaction of the surface with the gas and results in a smaller net heat of adsorption.

This total heat of adsorption up to the monolayer ($\Delta H_m$) consists of a part due to the low energy sites (sites at the homogeneous part of the surface) plus the excess attributed to the heterogeneity and the sum of the lateral interactions up to the monolayer which can be measured from the heat of adsorption curves at the monolayer. For the $BaSO_4$-$N_2$ system (Fig. 4), it is approximately equal to the heat of condensation ($\Delta H_s$) of $N_2$(56.96 ergs/cm$^2$). Therefore, the total measured net heat of adsorption [total heat (experimental) - heat of condensation] is equal to the net heat of adsorption on the homogeneous part of the surface as calculated by the B.E.T. constant C plus the net heat due to the heterogeneity of the surface. The contribution to the total heat of adsorption by the heterogeneity of the surface should be progressively decreased by the preadsorbate until it is very small compared to that of the lateral interactions and smooth part of the surface or zero. This will, of course, depend on the effectiveness of the preadsorbate and on the nature of surface. If the heterogeneity of $BaSO_4$ is due primarily to the cavities and if the preadsorbate does, indeed, cover them, then the contribution of the heterogeneity could be eliminated entirely. Therefore,

$$(\Delta H_m - \Delta H_s)^{\theta_{\|}}_{measured} = (\Delta H_m - \Delta H_s)^{\theta_{\|}}_{B.E.T.} + E_N^{\theta_{\|}}. \qquad (1)$$

$\theta_{\|}$ goes from 0 to 1. The results are shown in Table 3 for the $BaSO_4$-$N_2$ system as calculated from the data of columns 4 and 5 of Table 2. Initially

Table 3.

The net heats $\overline{Q}(\theta)$, $\overline{Q}_{B.E.T}$, and $E_N$ calculated from Table 2 and Equation 1.

| | $(\Delta H-\Delta H_s)_{exp} = \overline{Q}(\theta)$ $\frac{ergs}{cm^2}$ | $(\Delta H-\Delta H_s)_{B.E.T.} = \overline{Q}$ $\frac{ergs}{cm^2}$ | $E_N$ $\frac{ergs}{cm^2}$ |
|---|---|---|---|
| | 66.060 | 25.46 | 40.60 |
| A | 41.450 | 31.86 | 9.59 |
| | 55.18 | 28.00 | 27.180 |
| | 29.62 | 18.730 | 10.890 |
| B | 31.06 | 25.110 | 5.95 |
| | 26.30 | 20.380 | 5.920 |
| | 27.540 | 22.700 | 4.840 |
| C | 19.100 | 19.200 | - .100 |
| | 18.270 | 16.510 | 1.760 |
| D | 23.24 | 22.700 | .44 |
| | 19.100 | 19.200 | - .100 |

the contribution of heterogeneity to the total net heat measured for sample B at $\theta_{||} = 0$ is only 23% of the total; whereas, it is 62% and 49% for sample S2 and sample S1, respectively. The error on these heats is $\pm 2.1$ ergs/cm$^2$. The contributions to the total heat of adsorption due to the heterogeneity of the surface (column 3 of Table 3) are obviously different in magnitude for the three samples as a function of the fraction covered $\theta_{||}$. Its effect, however, is essentially zero for all three samples after $\theta_{||} = 60\%$. This is a very <u>interesting</u> and <u>meaningful</u> result. Note also (Table 3) that after $\theta_{||} = 60\%$ the net heats of adsorption ($\overline{Q}$) are approximately the same for the two samples which received the same preparation (S1 and S2); that it, $(18.27 \pm 2.1)$ ergs/cm$^2$. The third sample (B) is also within this range, $(23.24 \pm 2.1)$ ergs/cm$^2$. The B.E.T. heats ($\overline{Q}_{B.E.T.}$) which are a measure of the homogeneous part of the surface are also of the same relative magnitude. These results indicate that an appreciable part of the heterogeneity of the $BaSO_4$ samples as prepared in this study may be caused by the presence of these macroscopic defects (cavities) on its surface which are rendered inoperative by the presence of the stearic acid. It is not too often that surface nonuniformity can be attributed to any one defect. This is not to say that the $BaSO_4$ powders do not contain other imperfections; indeed, their number may be much larger than the cavities. However, if very small or very nonenergetic, their contribution to the surface area or to the energy of interaction should be negligible. This definitely seems to be the case with the $BaSO_4$ powders. The information presented in tabular form in Table 3 is also shown graphically in Fig. 5. Obviously sample B is the

more homogeneous of the three samples. $\overline{Q}(\theta)$ and $\overline{Q}_{B.E.T.}$ are plotted versus $\theta_{\parallel}$ and not $\theta_{\perp}$ since the analysis of the surface energy variation will be done for the parallel orientation only.

D. Conclusions from the Basic Results on $BaSO_4$ and $TiO_2$[2]

The net measured heat of adsorption ($\overline{Q}$), net heat from the B.E.T. theory ($\overline{Q}_{B.E.T.}$), and net heterogeneous heat ($E_N$) have been given for the $BaSO_4$ samples and the $TiO_2$ sample.[2] The results for $\overline{Q}$ and $\overline{Q}_{B.E.T.}$ were also given in graphical form in Figs. 5 and 8.[2] The most significant difference between the $TiO_2$-$N_2$ system and that of the $BaSO_4$-$N_2$ is that the contribution due to the heterogeneous portion of the surface is not eliminated for $TiO_2$.[2]

It is very interesting to note that $\overline{Q}_{B.E.T.}$ for the combination $TiO_2$-stearic acid surface is very similar in magnitude to $\overline{Q}_{B.E.T.}$ for $BaSO_4$-stearic acid film once the heat of adsorption remains constant with pre-adsorbate coverage; that is, around 19 ergs/cm$^2$. Bruaneur[8] points out the heat of adsorption of the homogeneous part of the surface does not change much even from adsorbent to adsorbent. It is comforting to observe this well-known fact. The predominate forces between a covered surface and a gas should be of a dispersion type, and dispersion forces between unlike atoms are usually of the same magnitude. Muller[9] found that the energy of interaction due to dispersion forces of a helium atom with an argon crystal is about the same as that of a helium atom with a titanium dioxide crystal. Lenel[10] found the dispersion force for argon on potassium chloride, potassium iodide, lithium fluoride, and cesium chloride to be about the same magnitude also. Therefore, this excellent agreement may be something more than fortuitous.

Finally, the results of net heats of adsorption as a function of the preadsorbate for both the $BaSO_4$-$N_2$ and $TiO_2$-$N_2$ systems up to the monolayer coverage indicate that $BaSO_4$ is more heterogeneous than $TiO_2$. The heterogeneity of $BaSO_4$ is due to large macroscopic cavities which are filled in by the preadsorbate effectively removing them and replacing them by a planar surface composed of stearic acid molecules and $BaSO_4$ molecules.

In the case of $TiO_2$ the observed heterogeneity is due to differing electrostatic forces on the surface which are caused by sharp points and many-sided sites. The preadsorbate only reduced their effect to the point where the ever present dispersion forces which were initially not as large as the electrostatic forces become more important.

Finally, the magnitude of the net heats for total coverage ($\theta_{\parallel} \geq 100\%$) is the same within experimental error for the three $BaSO_4$ samples, around 19 ergs/cm$^2$ (row D, column 1 of Table 3). This is experimental evidence for the fact that the combination ($BaSO_4$ + stearic acid) has a constant surface energy as was assumed in deriving the necessary equations for the relative energy distribution.[1]

## III. RELATIVE SURFACE ENERGY DISTRIBUTION FROM THE BASIC RESULTS OF THE NET HEAT OF ADSORPTION [$\overline{Q}(\theta)$]

### A. Relative Distribution for $BaSO_4$ Samples

We can now use the results of the net heat of adsorption $\overline{Q}(\theta)$ as a function of $\theta$ (Fig. 5) to calculate the relative distribution of energy $\epsilon_S(\theta) / \overline{\epsilon}_S(0)$ on the $BaSO_4$ samples. We will transform our knowledge of the variation of the net heat $\overline{Q}(\theta)$ with preadsorbed coverage into the relative surface energy distribution.

All the terms have been rigorously defined in a previous paper.[1] The values of $\theta$ used will be those calculated assuming a parallel orientation for the long-chain fatty acid. This choice has been justified by both theoretical and experimental considerations.[2] $\overline{Q}(\theta)$ is related to the energy of adhesion by the following equation,

$$\Delta E^2_{SL} = - \overline{Q}(\theta) + 2\epsilon_L \tag{2}$$

and to $\overline{\epsilon}_S(\theta)$, where $\theta$ goes from 0 to 1 by the expression for $\Phi$,

$$\Phi = \frac{(-\overline{Q}(\theta) + 2\epsilon_L)}{[4\epsilon_L\overline{\epsilon}_S(\theta)]^{1/2}} \tag{3}$$

The change in $\overline{\epsilon}_S(\theta)$ from the initial $\epsilon_S(0)$ was calculated using the experimental results for $\overline{Q}(\theta)$ and the equation,

$$\frac{\overline{\epsilon}_S(\theta)}{\overline{\epsilon}_S(0)} = \frac{(\overline{Q}(\theta) + 2\epsilon_L)^2}{(-\overline{Q}(0) + 2\epsilon_L)^2} \tag{4}$$

The results for sample S1 are shown in Table 4.

Table 4.

Values of $\bar{\epsilon}_S(\theta) / \bar{\epsilon}_S(0)$ calculated by equation (4).

| $\theta_{\parallel}$ | $\bar{\epsilon}_S(\theta) / \bar{\epsilon}_S(0)$ |
|---|---|
| 0 | 1 |
| .27 | .842 |
| .60 | .634 |
| 1.16 | .634 |

Similar calculations were performed on sample S2 and sample B, and the results are plotted in Fig. 6. The ratio starts at 1 and decreases to a constant fraction.

The following equation,

$$\frac{\bar{\epsilon}_S(\theta)}{\bar{\epsilon}_S(\theta)} = 1 + \frac{2\,(1 - \theta)}{(-\bar{Q}(\theta) + 2\epsilon_L)} \frac{d\bar{Q}(\theta)}{d\theta} \qquad (5)$$

can be used to calculate the average surface energy at any covered fraction of the surface, $\epsilon_S(\theta)$, with respect to the average energy of the bare surface remaining $\bar{\epsilon}_S(\theta)$ once the derivative of the net heat $\bar{Q}(\theta)$ is known. The result for sample S1 is shown in column 4 of Table 5.

Table 5

The relative surface energy distribution of $BaSO_4$ calculated from net heat of adsorption measurements, as a function of preadsorbed stearic acid, at T = 83.9°K, sample S1.

| $\theta_{\parallel}$ (%) | $-\bar{Q}$ $\frac{ergs}{cm^2}$ | $\frac{d\bar{Q}}{d\theta}$ $\frac{ergs}{cm^2}$ | $\frac{\epsilon_S(\theta)}{\bar{\epsilon}_S(\theta)}$ | $\frac{\epsilon_S(\theta)}{\bar{\epsilon}_S(0)}$ |
|---|---|---|---|---|
| 0 | 55.18 | 144.70 | 4.480 | 4.480 |
| .27 | 26.30 | 59.10 | 2.59 | 2.175 |
| .60 | 19.10 | 0 | 1 | .63 |
| 1.16 | 19.10 | 0 | 1 | .63 |

The results for $\epsilon_S(\theta) / \bar{\epsilon}_S(\theta)$ for the three samples are shown in Fig. 7. The results when values of $\bar{\epsilon}_S(\theta)/ \bar{\epsilon}_S(0)$ and $\epsilon_S(\theta)/ \bar{\epsilon}_S(\theta)$ are combined, (that is, $\epsilon_S(\theta) / \bar{\epsilon}_S(0)$ ) are shown for the three $BaSO_4$ samples in Fig. 8.

For the two samples which received the same preparation (S1 and S2), approximately 10% of the surface had energies from 3 to 4-1/2 times greater than the average. A theoretical calculation on the influence of a cavity on adsorption energies (van der Waal's forces) has been treated by De Boer and Custers.[11] They found that the interaction energy is four times greater in a cavity of semicircular geometry than that of a molecularly smooth surface. Figure 8 is in qualitative agreement with this calculation since initially the interaction between $BaSO_4$ and the gas is believed to be due to such a cavity. Twenty percent of the two similar surfaces have energies approximately 2.5 times the average. The results also indicate that more than 50% of the surfaces have energies below the average value. Strong

attraction for these two $BaSO_4$ samples and some second phase is primarily due to roughtly 45% of the surface. The sample which received the longest heat treatment (B) is quite different. Only 10% of its surface has energies about 2 times the average. A large fraction (70%) of the surface has energies below the average. After 20% this surface is relatively homogeneous. After $\theta_{\|} = 60\%$, all three samples converge to an average value of approximately $1/2\bar{\epsilon}_S(0)$. The average total surface energy $[\bar{\epsilon}_S(0)]$ for each sample is different so that the absolute value of the surface energy for the homogeneous fraction of the surface will not be the same. However, it is interesting that the relative values are approximately equal for the homogeneous region, but considerably different in the heterogeneous part of the surface. There are sites on all three samples which have energies between 4.5 to 5 times the average surface energies. The distributions presented are definitely a function of the surface preparation used. A more efficient degassing technique (sputtering) could result in a distribution which has sites as high as 10 times the average.

## IV. CONCLUSIONS

Since this was the first attempt to measure the relative distribution of energy on $BaSO_4$, comparison with other work is not possible. However, from this work we have concluded that dispersion rather than electrostatic forces predominate on the surface of $BaSO_4$. Electrostatic surface forces are not appreciable for molecular crystals; that is, one whose lattice sites are occupied by molecules rather than atoms or non-atomic ions, of which $BaSO_4$ is a known example. The magnitude and shape of the measured heat of adsorption curves are consistent with this conclusion.

The heterogeneity observed is caused by the presence of surface cavities which initially make a contribution not only to the energy but also to the surface area of the powder. Progressive coating of the surface with the fatty acid tends to eliminate these cavities. This results in a more homogeneous surface and a decrease in surface area. For all three samples of $BaSO_4$, 60% of the surface was found to be heterogeneous.

For the two similar samples approximately 10% of the surface had energies from 3 to 4-1/2 times greater than the average. This increase in the energy is attributed to the cavities and this proposition is supported by a theoretical calculation on the influence of a cavity on adsorption energies which found the interaction to be four times greater as measured in this work.

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## FIGURE CAPTIONS

Fig. 1 Adsorption isotherm of nitrogen with the fraction of surface covered with stearic acid ($\theta$) as parameter at T = 77.5°K.

Fig. 2 B.E.T. plots with the fraction of surface covered with stearic acid ($\theta$) as parameter.

Fig. 3 Surface area of $BaSO_4$ samples as a function of preadsorbed stearic acid ($\theta_{\|}$).

Fig. 4 Isosteric heat of adsorption of nitrogen versus moles adsorbed with the fraction of the surface covered with stearic acid as parameter, sample S1.

Fig. 5 The net experimental heat and the net B.E.T. heat as a function of $\theta_{\|}$ for the $BaSO_4$ samples.

Fig. 6 $\bar{\epsilon}_S(\theta) / \bar{\epsilon}_S(0)$ versus $\theta_{\|}$ for $BaSO_4$ samples.

Fig. 7 $\epsilon_S(\theta) / \bar{\epsilon}_S(\theta)$ versus $\theta_{\|}$ for $BaSO_4$ samples.

Fig. 8 $\epsilon_S(\theta) / \bar{\epsilon}_S(0)$ versus $\theta_{\|}$ for $BaSO_4$ samples.

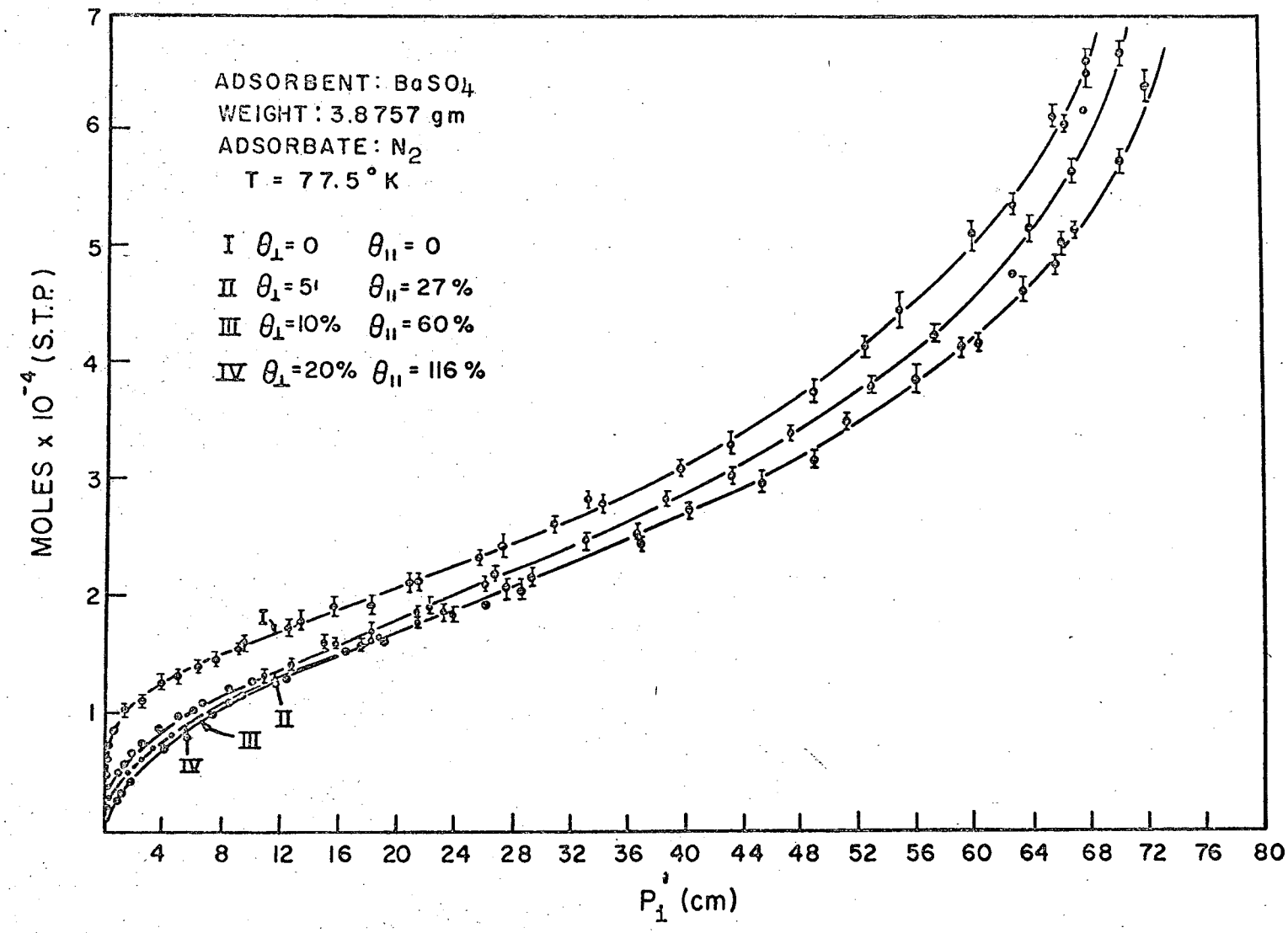
ADSORBENT: BaSO4
WEIGHT: 3.8757 gm
ADSORBATE: N2
T = 77.5 °K
I θ⊥ = 0 θ∥ = 0
II θ⊥ = 5% θ∥ = 27%
III θ⊥ = 10% θ∥ = 60%
IV θ⊥ = 20% θ∥ = 116%
MOLES x 10^-4 (S.T.P.)
P_i (cm)
I
II
III
IV
1
2
3
4
5
6
7
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80

Fig. 1

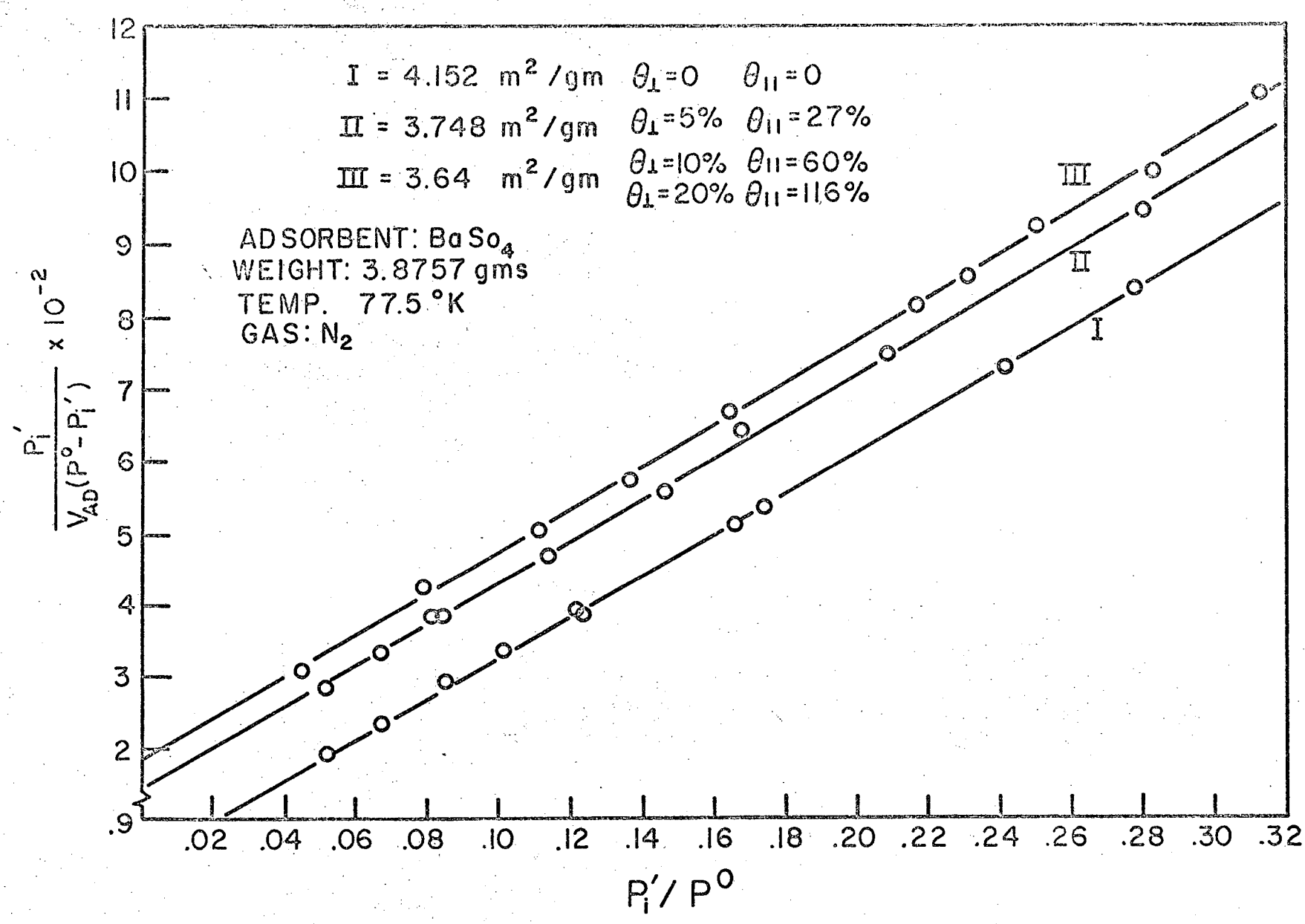
I = 4.152 m²/gm θ⊥=0 θ∥=0
II = 3.748 m²/gm θ⊥=5% θ∥=27%
III = 3.64 m²/gm θ⊥=10% θ∥=60%
θ⊥=20% θ∥=116%
ADSORBENT: BaSo4
WEIGHT: 3.8757 gms
TEMP. 77.5 °K
GAS: N2
III
II
I
12
11
10
9
8
7
6
5
4
3
2
.9
.02
.04
.06
.08
.10
.12
.14
.16
.18
.20
.22
.24
.26
.28
.30
.32
Pi'/P°
Pi' / VAD(P°-Pi') x 10⁻²

Fig. 2

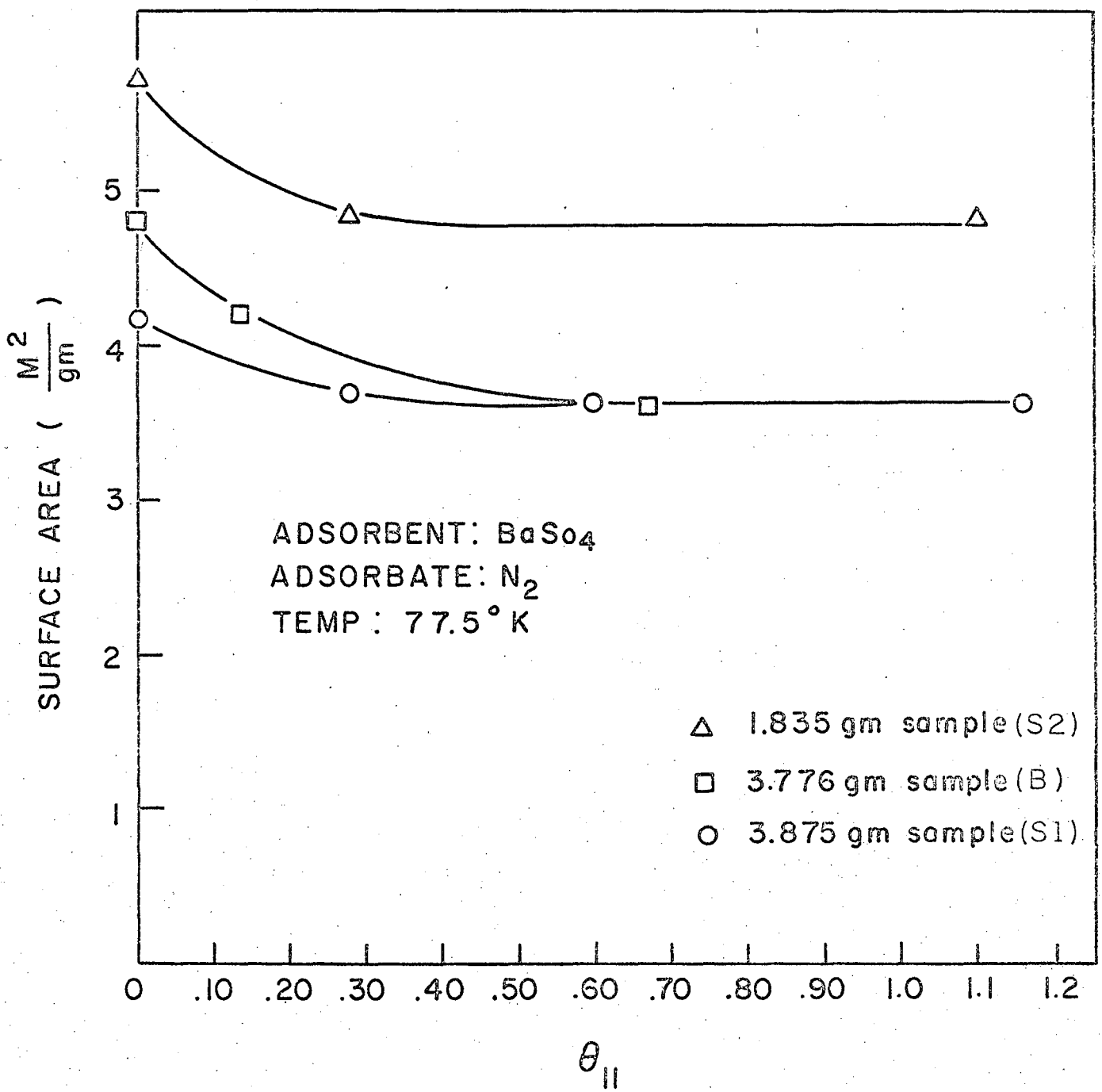
SURFACE AREA ( $\frac{M^2}{gm}$ )
5
4
3
2
1
ADSORBENT: $BaSo_4$
ADSORBATE: $N_2$
TEMP : 77.5° K
1.835 gm sample (S2)
3.776 gm sample (B)
3.875 gm sample (S1)
0
.10
.20
.30
.40
.50
.60
.70
.80
.90
1.0
1.1
1.2
$\theta_{II}$

Fig. 3

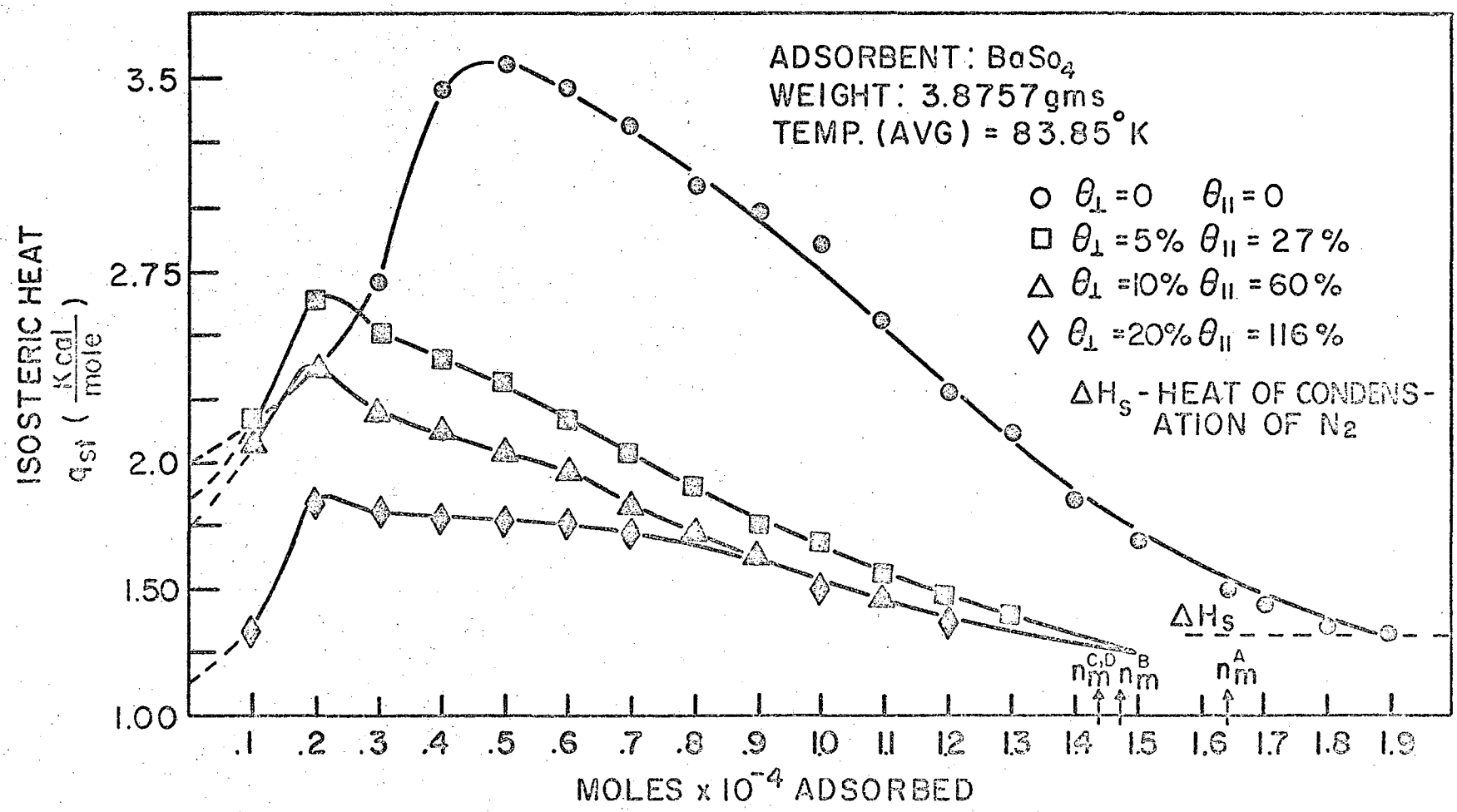
ADSORBENT: $BaSo_4$
WEIGHT: 3.8757 gms
TEMP. (AVG) = 83.85°K
○ $\theta_\perp = 0$ $\theta_\parallel = 0$
□ $\theta_\perp = 5\%$ $\theta_\parallel = 27\%$
△ $\theta_\perp = 10\%$ $\theta_\parallel = 60\%$
◇ $\theta_\perp = 20\%$ $\theta_\parallel = 116\%$
$\Delta H_s$ - HEAT OF CONDENSATION OF $N_2$
$\Delta H_s$
$n_m^{C,D}$
$n_m^B$
$n_m^A$
ISOSTERIC HEAT
$q_{st}$ ( $\frac{K\,cal}{mole}$ )
3.5
2.75
2.0
1.50
1.00
.1 .2 .3 .4 .5 .6 .7 .8 .9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9
MOLES x $10^{-4}$ ADSORBED

Fig. 4

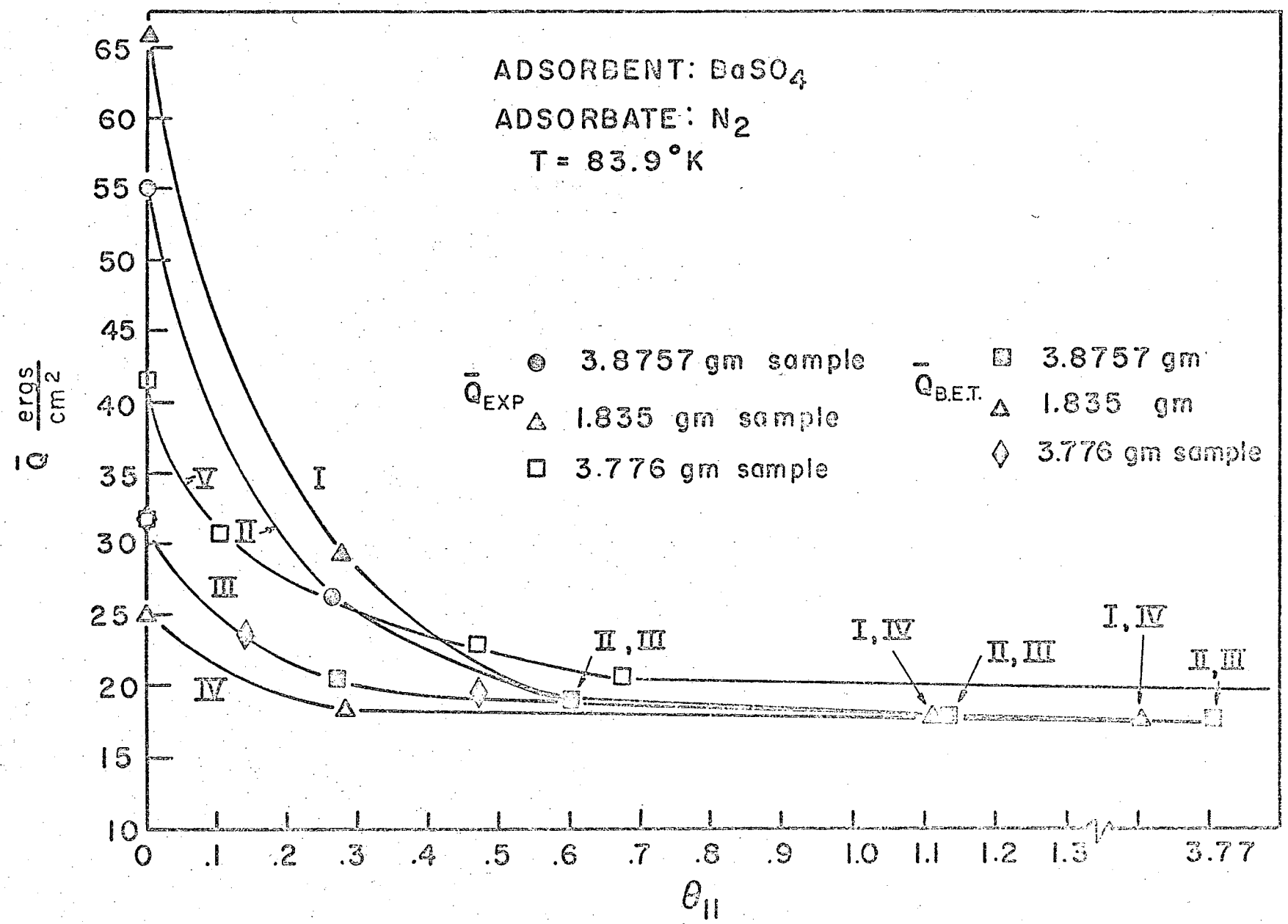
ADSORBENT: $BaSO_4$
ADSORBATE: $N_2$
T = 83.9°K
$\bar{Q}_{EXP}$
3.8757 gm sample
1.835 gm sample
3.776 gm sample
$\bar{Q}_{B.E.T.}$
3.8757 gm
1.835 gm
3.776 gm sample
$\bar{Q}$ $\frac{ergs}{cm^2}$
$\theta_{II}$
I
II
III
IV
V
I, IV
II, III
65
60
55
50
45
40
35
30
25
20
15
10
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
3.77

Fig. 5

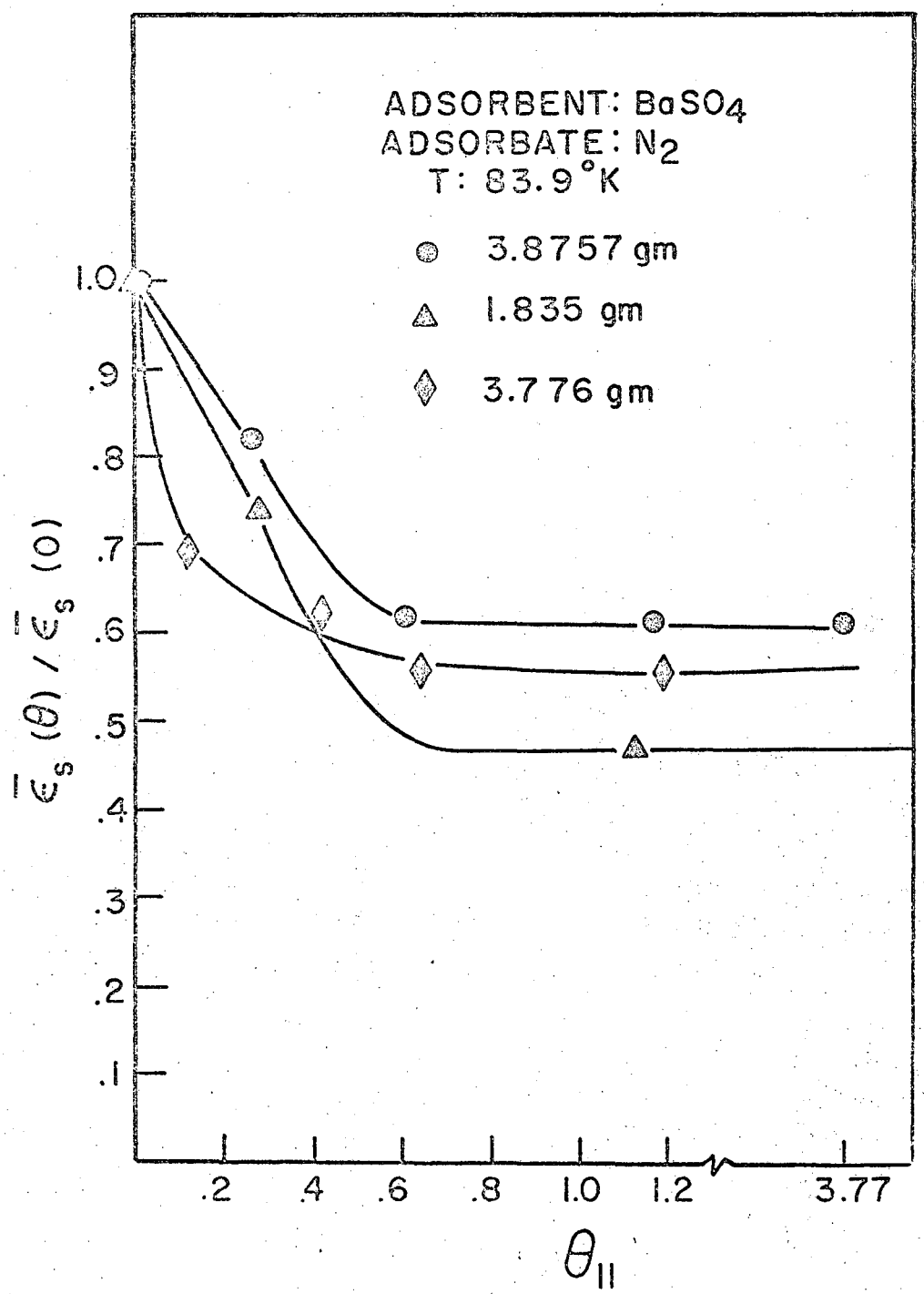
ADSORBENT: BaSO4
ADSORBATE: N2
T: 83.9 °K
3.8757 gm
1.835 gm
3.776 gm
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
$\bar{\epsilon}_s(\theta) / \bar{\epsilon}_s(0)$
.2
.4
.6
.8
1.0
1.2
3.77
$\theta_{II}$

Fig. 6

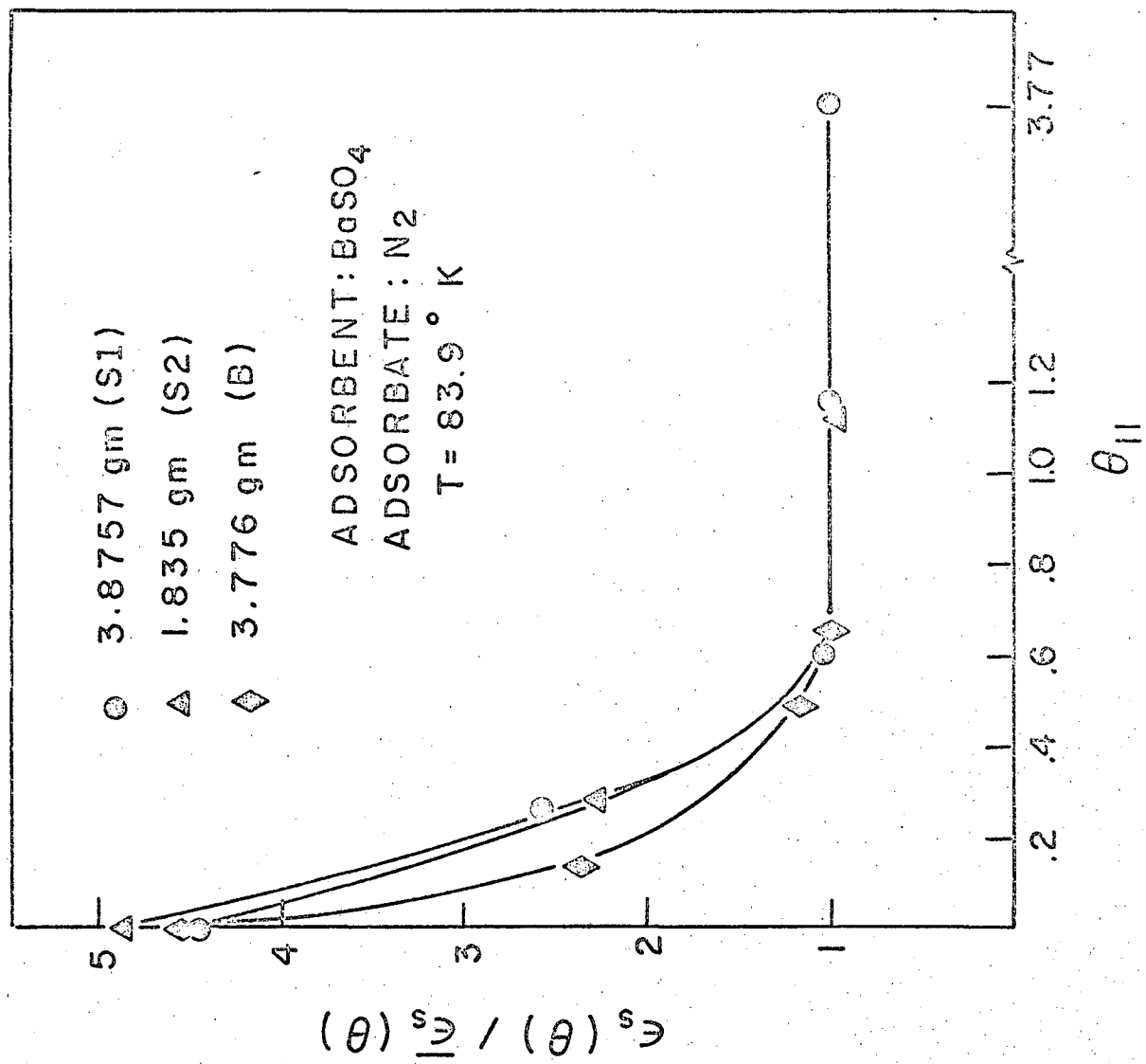
3.8757 gm (S1)
1.835 gm (S2)
3.776 gm (B)
ADSORBENT: BaSO4
ADSORBATE : N2
T= 83.9 ° K
5
4
3
2
1
.2
.4
.6
.8
1.0
1.2
3.77
θ11
εs (θ) / ε̄s (θ)

Fig. 7

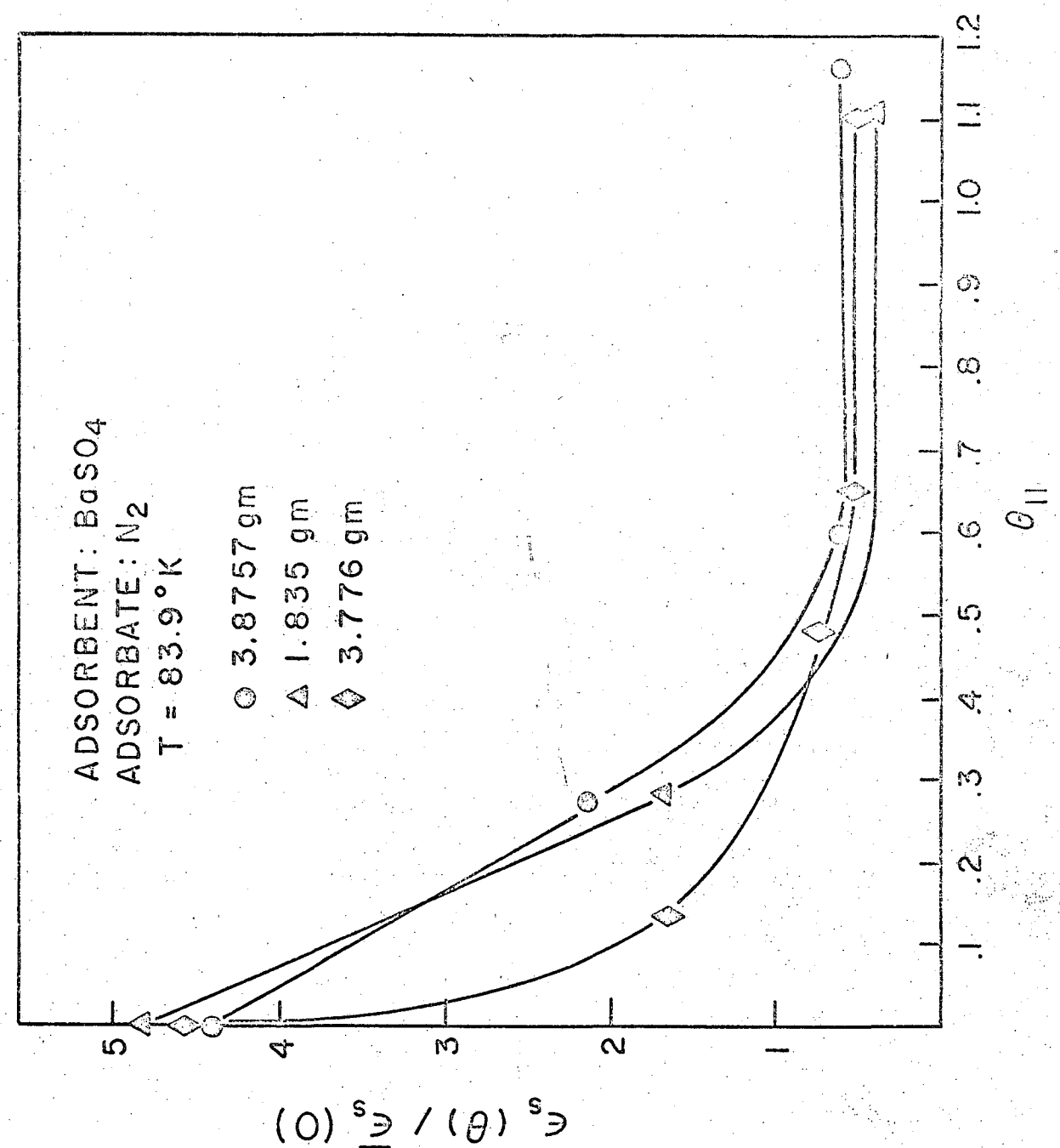
ADSORBENT: BaSO4
ADSORBATE: N2
T = 83.9°K
3.8757 gm
1.835 gm
3.776 gm
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
θII
1
2
3
4
5
εs (θ) / ε̄s (0)

Fig. 8

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