

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

THE RELATIVE DISTRIBUTION OF ENERGY ON THE BaSO<sub>4</sub> SURFACE: PART III

### Permalink

<https://escholarship.org/uc/item/49q4x2c8>

### Authors

Morabito, J.M.

Duby, P.F.

### Publication Date

1968-02-01

*eg. 2*

# University of California

## Ernest O. Lawrence Radiation Laboratory

THE RELATIVE DISTRIBUTION OF ENERGY  
ON THE BaSO<sub>4</sub> SURFACE: PART III

J. M. Morabito, Jr. and P. F. Doby

February 1968

**TWO-WEEK LOAN COPY**

This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545

Berkeley, California

RECEIVED  
LIBRARY  
UNIVERSITY OF CALIFORNIA

LIBRARY AND  
DOCUMENTS SERVICE

31

UCRL-17819  
*eg. 2*

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to: J. Phys. Chem.

UCRL-17819  
Preprint

UNIVERSITY OF CALIFORNIA  
Lawrence Radiation Laboratory  
Berkeley, California  
AEC Contract No. W-7405-eng-48

THE RELATIVE DISTRIBUTION OF ENERGY ON  
THE  $\text{BaSO}_4$  SURFACE: PART III

J. M. Morabito, Jr.

and

P. F. Doby

February 1968

THE RELATIVE DISTRIBUTION OF ENERGY ON  
THE BaSO<sub>4</sub> SURFACE: PART III

J. M. Morabito, Jr.<sup>†</sup>  
University of Pennsylvania, Philadelphia, Pa.,

and

P. F. Doby  
Columbia University, New York City, N. Y.

ABSTRACT

This is the first attempt to measure the relative distribution of energies on the surface of BaSO<sub>4</sub>. 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

<sup>†</sup> Present affiliation: Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California.

surface of  $\text{BaSO}_4$ ; this is reasonable for a molecular crystal such as  $\text{BaSO}_4$ .

I. INTRODUCTION

In a recent publication<sup>1</sup> the theoretical description of the relative distribution of energy on a solid surface was derived and applied to the  $\text{TiO}_2$  surface. Very little has been published on the surface properties of  $\text{BaSO}_4$ , and the nature of its heterogeneity is unknown. For this reason a detailed adsorption study of the  $\text{BaSO}_4\text{-N}_2$  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  $\text{BaSO}_4$ .

## II. EXPERIMENTAL

The type of apparatus used and preparation of the bare  $\text{BaSO}_4$  samples prior to the adsorption measurements and its coating with stearic acid was exactly the same as that of the  $\text{TiO}_2$  study.<sup>2</sup> Three samples of  $\text{BaSO}_4$  were investigated. Two of the samples (designated as S1 and S2) were subjected to the same heat treatment ( $600^\circ\text{C}$  for 6 days) and the third (sample B) received a prolonged heat treatment ( $600^\circ\text{C}$  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,  $\text{BaSO}_4$  is known to contain water coprecipitated with  $\text{BaSO}_4$  molecules and held in pockets in the crystallites;<sup>3</sup> Three molecules of water substitute for each  $\text{BaSO}_4$  ion pair in the crystal lattice.\* Wu and Copeland<sup>4</sup> have shown that this water cannot be completely removed at any temperature below  $600^\circ\text{C}$  and  $10^{-6}$  mm Hg pressure. They fail to point out, however, that at these temperatures  $\text{BaSO}_4$  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 ( $500^\circ - 600^\circ\text{C}$ ) 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  $86\text{\AA}^3$  (one-quarter of the unit cell) and three water molecules about  $90\text{\AA}^3$ .



### III. RESULTS AND DISCUSSION

#### A. Adsorption Isotherms

The effect of preadsorbed stearic acid on the nitrogen adsorption isotherm of  $\text{BaSO}_4$  is similar to that of  $\text{TiO}_2$ . Typical isotherms for bare and coated conditions at  $77.5^\circ\text{K}$  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  $77.5^\circ\text{K}$  and  $90.2^\circ\text{K}$ . 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<sup>2</sup> 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  $P_1/P_0 = .05$  to  $.35$  as shown in Fig. 2.  $P_1^s$  is the equilibrium pressure and  $P_0$  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 "subtraction" lattice.<sup>3</sup> The effect of this removal on the surface is not certain, but it has been suggested by Wu and Copeland<sup>4</sup> 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.<sup>4</sup> 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 area 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.  $\text{BaSO}_4$  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  $22.29\text{\AA}^2$  and the area of a nitrogen molecule is  $16.2\text{\AA}^2$ , they will be occupied 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.<sup>5,6</sup> 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<sup>7</sup> 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,<sup>2</sup> 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	$\theta_{  }$ (%)	$\theta$ (%)	$\Delta H_m$ ( $\frac{\text{ergs}}{\text{cm}^2}$ ) Experimental total	$\Delta H_m$ ( $\frac{\text{ergs}}{\text{cm}^2}$ ) B. E. T.
A	S2	0	123.02	82.42
	B	0	98.41	88.820
	S1	0	112.140	88.820
B	S2	27.49	86.58	75.69
	B	13.21	88.02	82.07
	S1	26.98	83.26	77.34
C	S2			
	B	48.00	84.500	79.66
	S1	60.19	76.01	76.16
D	S2	112.35	75.23	73.92
	B	65.75	80.20	79.66
	S1	116.61	69.46	76.16

are available. This type of curve is not impossible for the  $\text{BaSO}_4\text{-N}_2$  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  $600^\circ$ ) 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 reveal its precise nature. In addition, the shape, orientation, true size, etc., of the cavities on the surface of  $\text{BaSO}_4$  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 accommodate 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  $\text{BaSO}_4\text{-N}_2$  system (Fig. 4), it is approximately equal to the heat of condensation ( $\Delta H_s$ ) of  $\text{N}_2$  ( $56.96 \text{ ergs/cm}^2$ ). 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  $\text{BaSO}_4$  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,

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

$\theta_{\parallel}$  goes from 0 to 1. The results are shown in Table 3 for the  $\text{BaSO}_4\text{-N}_2$  system as calculated from the data of columns 4 and 5 of Table 2. Initially



Table 3.

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

	$(\Delta H - \Delta H_s)_{\text{exp}} = \bar{Q}(\theta)$	$(\Delta H - \Delta H_s)_{B.E.T.} = \bar{Q}$	$E_N$
	$\frac{\text{ergs}}{\text{cm}^2}$	$\frac{\text{ergs}}{\text{cm}^2}$	$\frac{\text{ergs}}{\text{cm}^2}$
	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<sup>2</sup>. 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 interesting and meaningful result. Note also (Table 3) that after  $\theta_{||} = 60\%$  the net heats of adsorption ( $\bar{Q}$ ) are approximately the same for the two samples which received the same preparation (S1 and S2); that is,  $(18.27 \pm 2.1)$  ergs/cm<sup>2</sup>. The third sample (B) is also within this range,  $(23.24 \pm 2.1)$  ergs/cm<sup>2</sup>. The B.E.T. heats ( $\bar{Q}_{B.E.T.}$ ) 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<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> 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.  $\bar{Q}(\theta)$  and  $\bar{Q}_{B.E.T.}$  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<sub>4</sub> and TiO<sub>2</sub><sup>2</sup>

The net measured heat of adsorption ( $\bar{Q}$ ), net heat from the B.E.T. theory ( $\bar{Q}_{B.E.T.}$ ), and net heterogeneous heat ( $E_N$ ) have been given for the BaSO<sub>4</sub> samples and the TiO<sub>2</sub> sample.<sup>2</sup> The results for  $\bar{Q}$  and  $\bar{Q}_{B.E.T.}$  were also given in graphical form in Figs. 5 and 8.<sup>2</sup> The most significant difference between the TiO<sub>2</sub>-N<sub>2</sub> system and that of the BaSO<sub>4</sub>-N<sub>2</sub> is that the contribution due to the heterogeneous portion of the surface is not eliminated for TiO<sub>2</sub>.<sup>2</sup>

It is very interesting to note that  $\bar{Q}_{B.E.T.}$  for the combination TiO<sub>2</sub>-stearic acid surface is very similar in magnitude to  $\bar{Q}_{B.E.T.}$  for BaSO<sub>4</sub>-stearic acid film once the heat of adsorption remains constant with pre-adsorbate coverage; that is, around 19 ergs/cm<sup>2</sup>. Bruaneur<sup>8</sup> 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<sup>9</sup> 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<sup>10</sup> 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  $\text{BaSO}_4\text{-N}_2$  and  $\text{TiO}_2\text{-N}_2$  systems up to the monolayer coverage indicate that  $\text{BaSO}_4$  is more heterogeneous than  $\text{TiO}_2$ . The heterogeneity of  $\text{BaSO}_4$  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  $\text{BaSO}_4$  molecules.

In the case of  $\text{TiO}_2$  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 ( $\theta_{||} \geq 100\%$ ) is the same within experimental error for the three  $\text{BaSO}_4$  samples, around  $19 \text{ ergs/cm}^2$  (row D, column 1 of Table 3). This is experimental evidence for the fact that the combination ( $\text{BaSO}_4$  + stearic acid) has a constant surface energy as was assumed in deriving the necessary equations for the relative energy distribution.<sup>1</sup>

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

A. Relative Distribution for BaSO<sub>4</sub> Samples

We can now use the results of the net heat of adsorption  $\bar{Q}(\theta)$  as a function of  $\theta$  (Fig. 5) to calculate the relative distribution of energy  $\epsilon_S(\theta) / \bar{\epsilon}_S(0)$  on the BaSO<sub>4</sub> samples. We will transform our knowledge of the variation of the net heat  $\bar{Q}(\theta)$  with preadsorbed coverage into the relative surface energy distribution.

All the terms have been rigorously defined in a previous paper.<sup>1</sup> 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.<sup>2</sup>  $\bar{Q}(\theta)$  is related to the energy of adhesion by the following equation,

$$\Delta E_{SL}^2 = -\bar{Q}(\theta) + 2\epsilon_L \quad (2)$$

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

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

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

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

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).

$\theta_{  }$	$\bar{\epsilon}_S(\theta) / \bar{\epsilon}_S(0)$
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,

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

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  $\text{BaSO}_4$  calculated from net heat of adsorption measurements, as a function of preadsorbed stearic acid, at  $T = 83.9^\circ\text{K}$ , sample S1.

$\theta_{\parallel}$ (%)	$-\bar{Q} \frac{\text{ergs}}{\text{cm}^2}$	$\frac{d\bar{Q}}{d\theta} \frac{\text{ergs}}{\text{cm}^2}$	$\frac{\epsilon_S(\theta)}{\bar{\epsilon}_S(\theta)}$	$\frac{\epsilon_S(\theta)}{\bar{\epsilon}_S(0)}$
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  $\text{BaSO}_4$  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.<sup>11</sup> 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  $\text{BaSO}_4$  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  $\text{BaSO}_4$  samples and some second phase is primarily due to roughly 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  $\theta_{\parallel} = 60\%$ , 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  $\text{BaSO}_4$ , 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  $\text{BaSO}_4$ . 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  $\text{BaSO}_4$  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  $\text{BaSO}_4$ , 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.

ACKNOWLEDGEMENTS

The authors wish to sincerely thank L. A. Girifalco for many helpful discussions.

This work was supported by the National Institute of Health and in part by the United States Atomic Energy Commission.

REFERENCES

1. J. M. Morabito, Jr. and P. F. Doby, this journal.
2. J. M. Morabito, Jr., P. F. Doby, and L. A. Girifalco, this journal.
3. G. Walton and G. H. Walden, Jr., J. Am. Chem. Soc. 68, 1750 (1946).
4. Y. C. Wu and L. E. Copeland, Solid Surfaces and the Gas-Solid Interface, in Advances in Chemistry, Vol. 33 (American Chemical Society, Washington, D.C., 1961).
5. J. G. Aston and H. Chon, J. Phys. Chem. 63, 1015 (1961).
6. T. N. Rhodin, Jr., J. Am. Chem. Soc. 72, 4343, 5691 (1950).
7. S. Brunauer, Solid Surfaces and the Gas-Solid Interface, in Advances in Chemistry, Vol. 33 (American Chemical Society, Washington, D.C., 1961), p. 7.
8. S. Brunauer, Adsorption of Gases and Vapors (Princeton University Press, Princeton, New Jersey, 1943).
9. A. Muller, Proc. Roy. Soc. (London) A154, 624 (1936).
10. F. V. Lenel, Z. Phys. Chem. B23, 379 (1933).
11. J. H. DeBoer and J. F. H. Custers, Uber die Natur der Adsorptionskrafte Zeitschrift fur Physikalische Chemie 25B, 225 (1934).

FIGURE CAPTIONS

- Fig. 1 Adsorption isotherm of nitrogen with the fraction of surface covered with stearic acid ( $\theta$ ) as parameter at  $T = 77.5^\circ\text{K}$ .
- Fig. 2 B.E.T. plots with the fraction of surface covered with stearic acid ( $\theta$ ) as parameter.
- Fig. 3 Surface area of  $\text{BaSO}_4$  samples as a function of preadsorbed stearic acid ( $\theta_{||}$ ).
- Fig. 4 Isothermic 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  $\text{BaSO}_4$  samples.
- Fig. 6  $\bar{\epsilon}_S(\theta) / \bar{\epsilon}_S(0)$  versus  $\theta_{||}$  for  $\text{BaSO}_4$  samples.
- Fig. 7  $\epsilon_S(\theta) / \bar{\epsilon}_S(\theta)$  versus  $\theta_{||}$  for  $\text{BaSO}_4$  samples.
- Fig. 8  $\epsilon_S(\theta) / \bar{\epsilon}_S(0)$  versus  $\theta_{||}$  for  $\text{BaSO}_4$  samples.

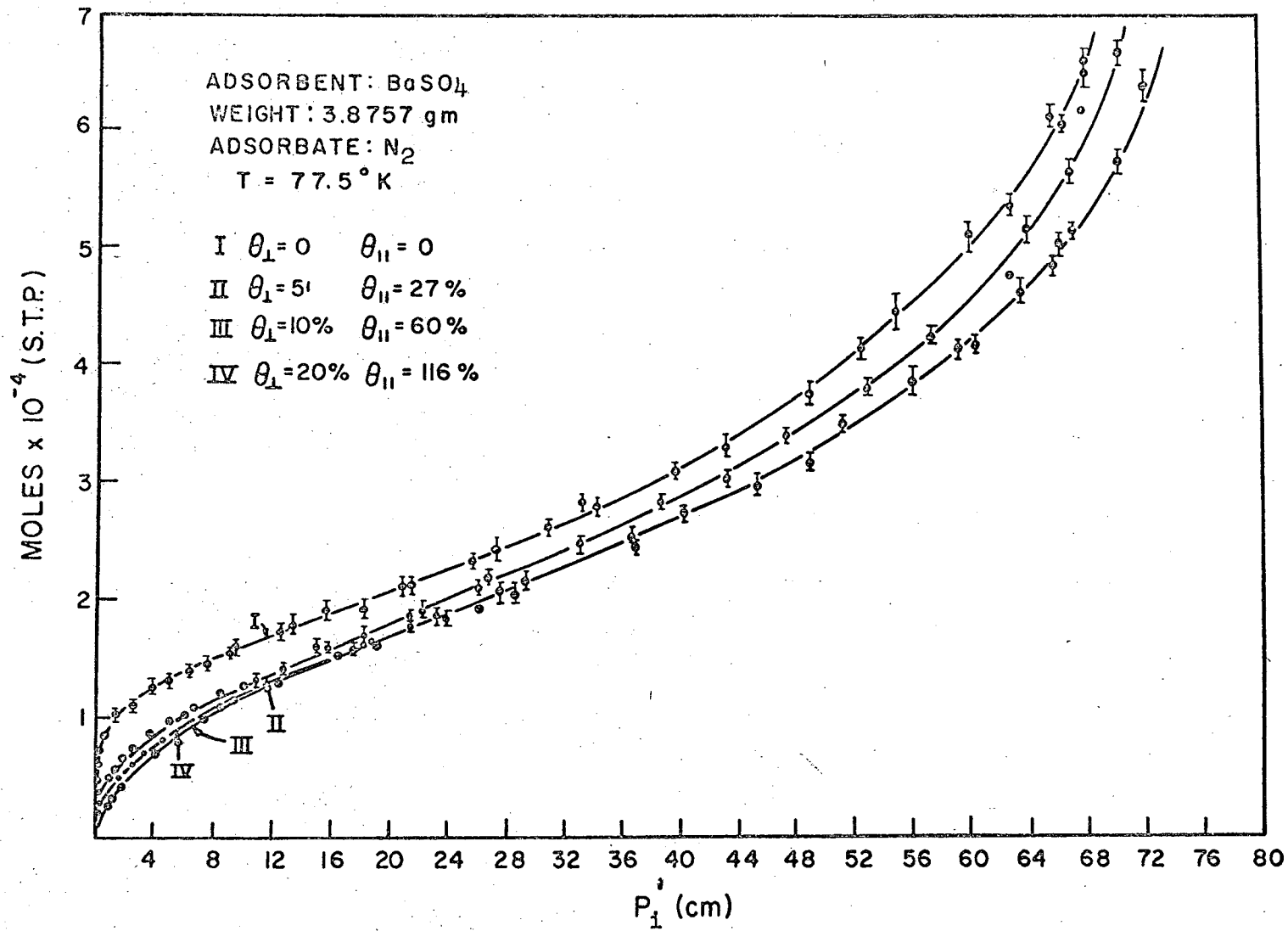


Fig. 1



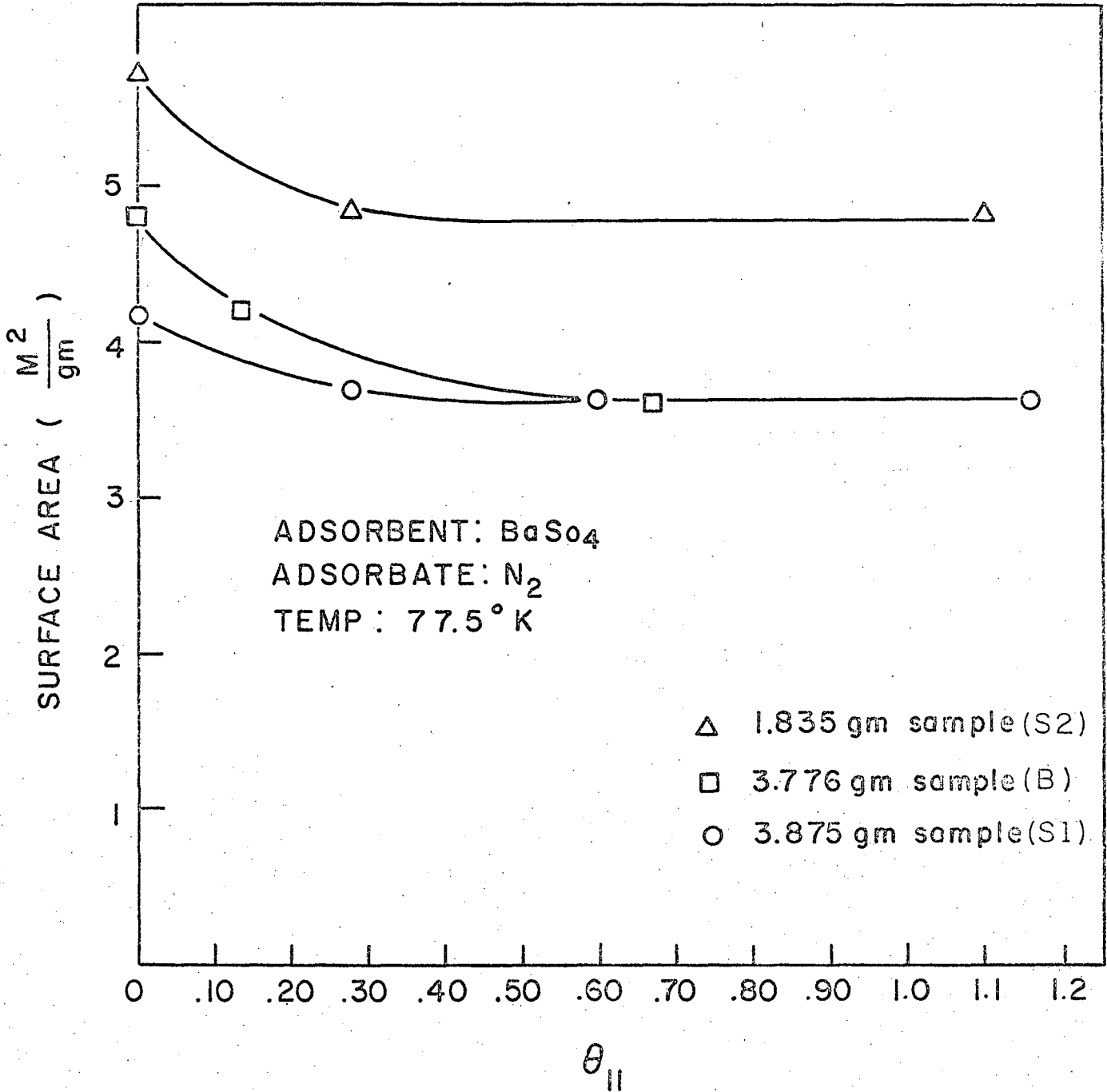


Fig. 3

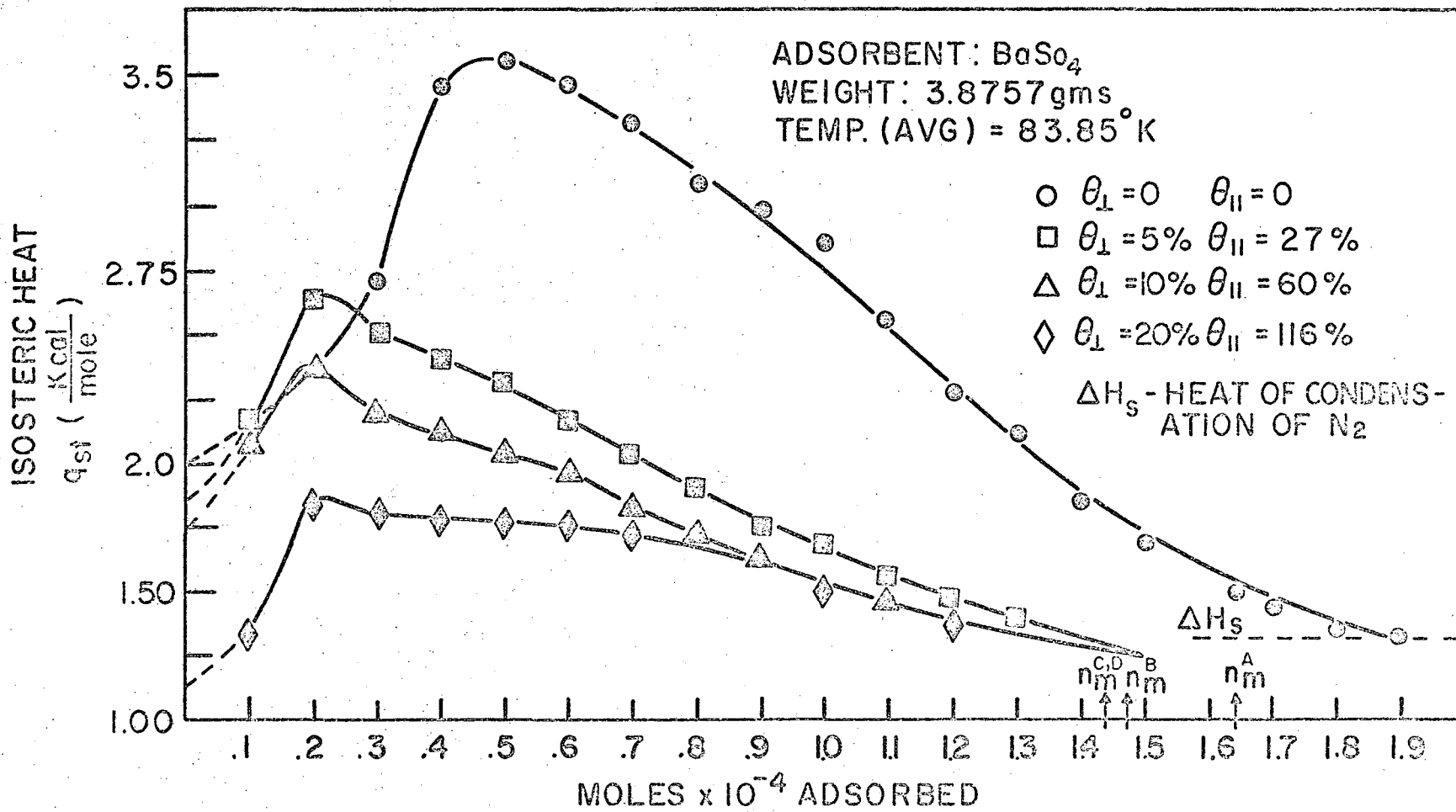


Fig. 4



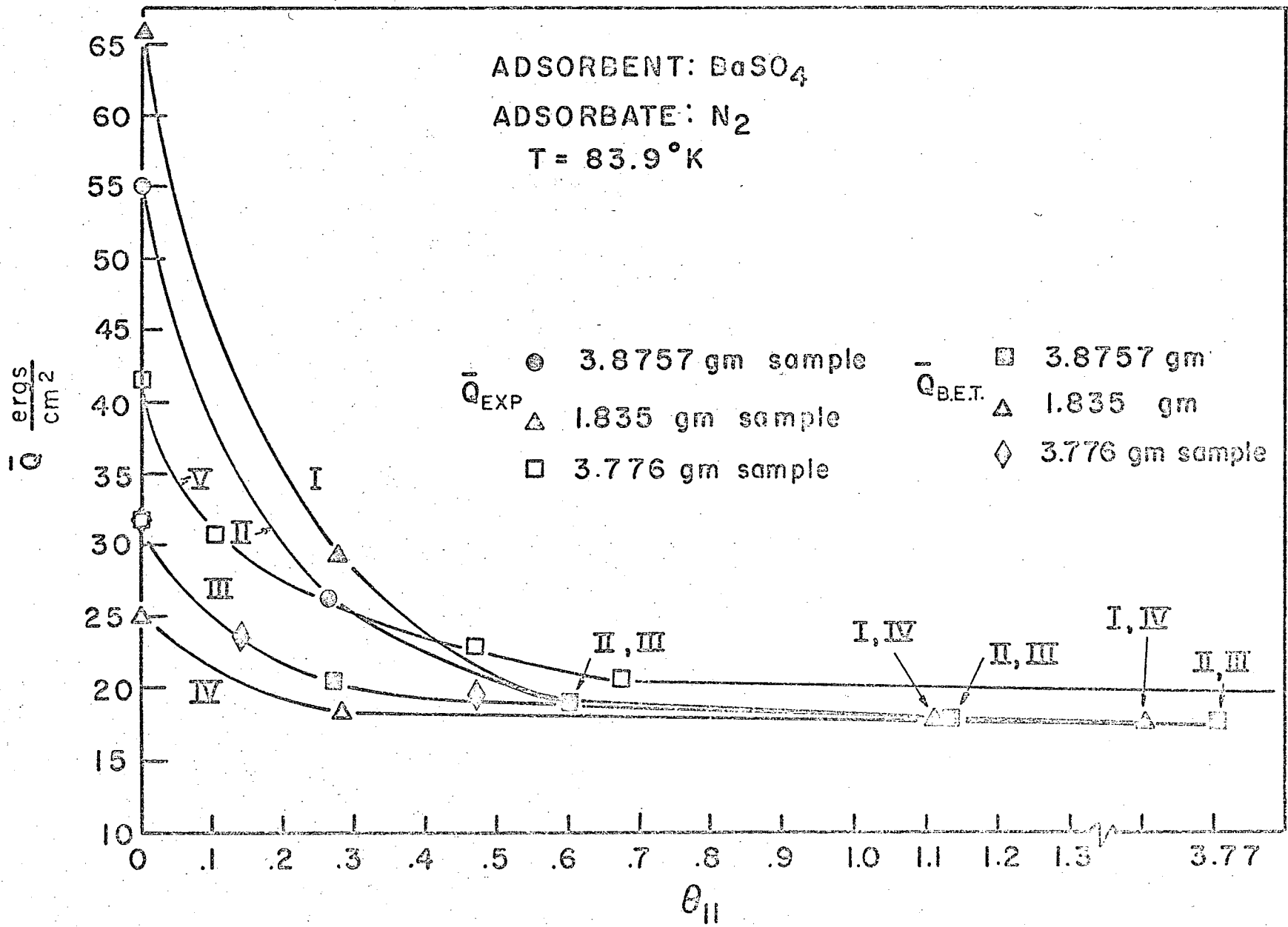


Fig. 5

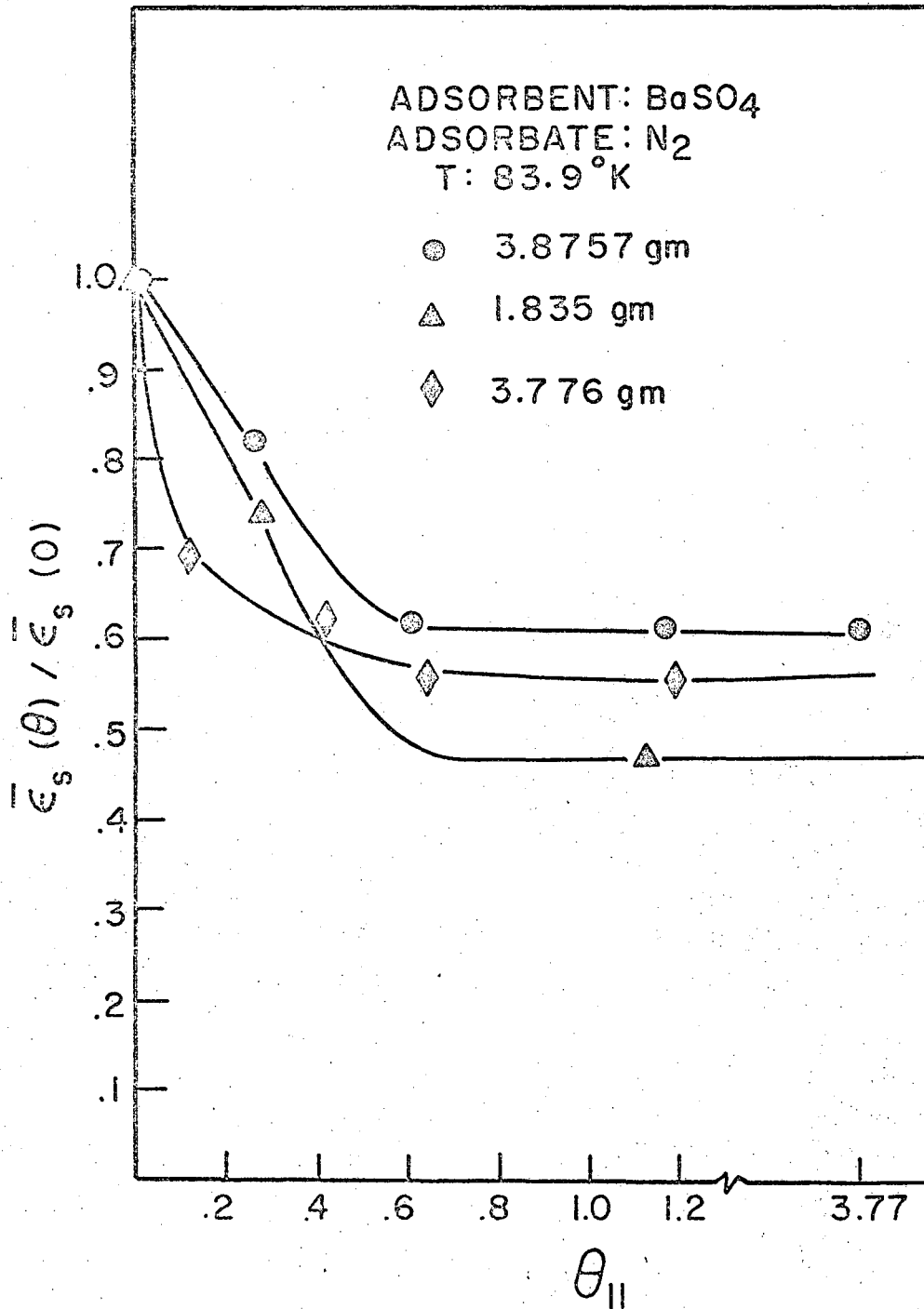


Fig. 6

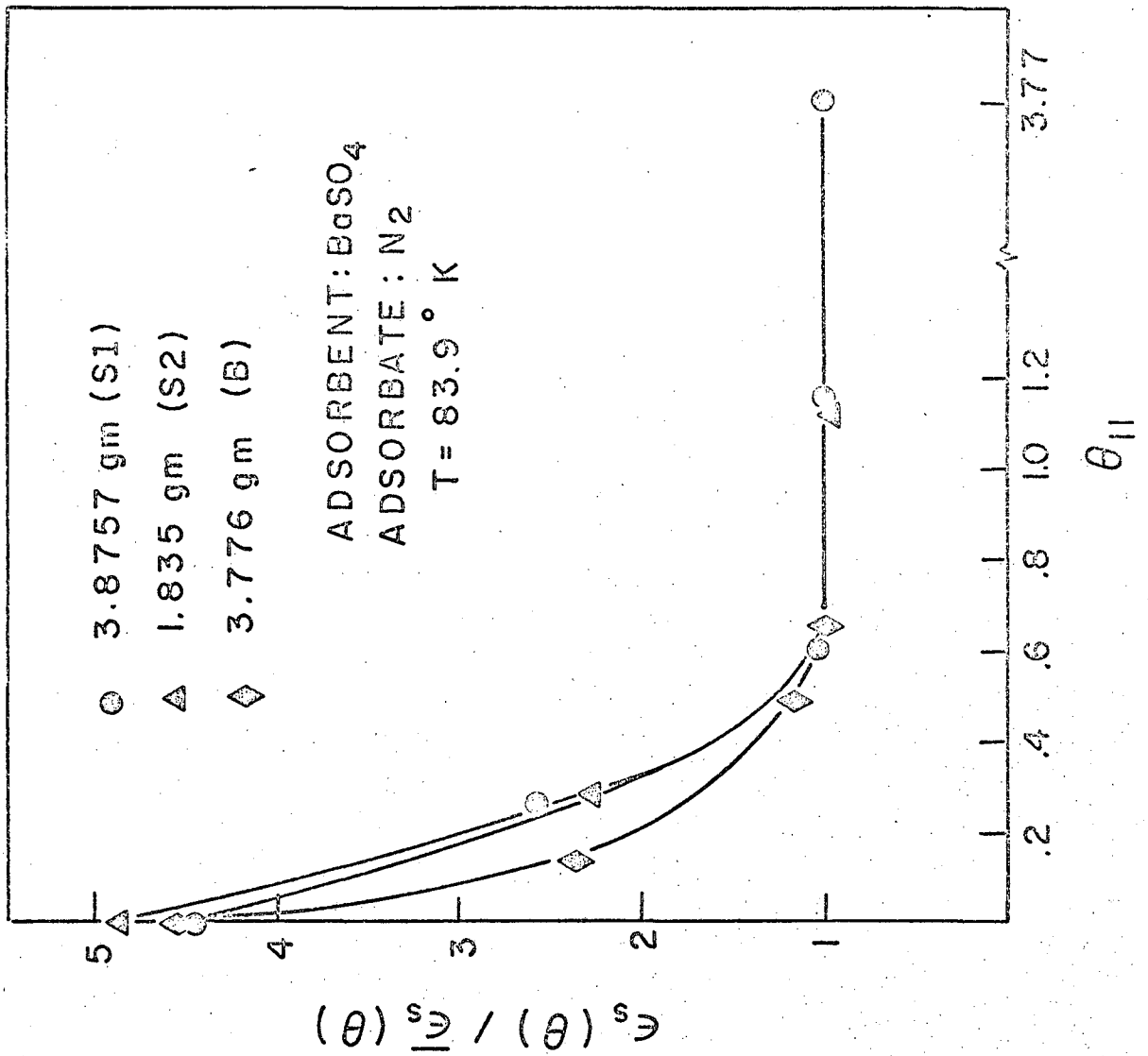


Fig. 7

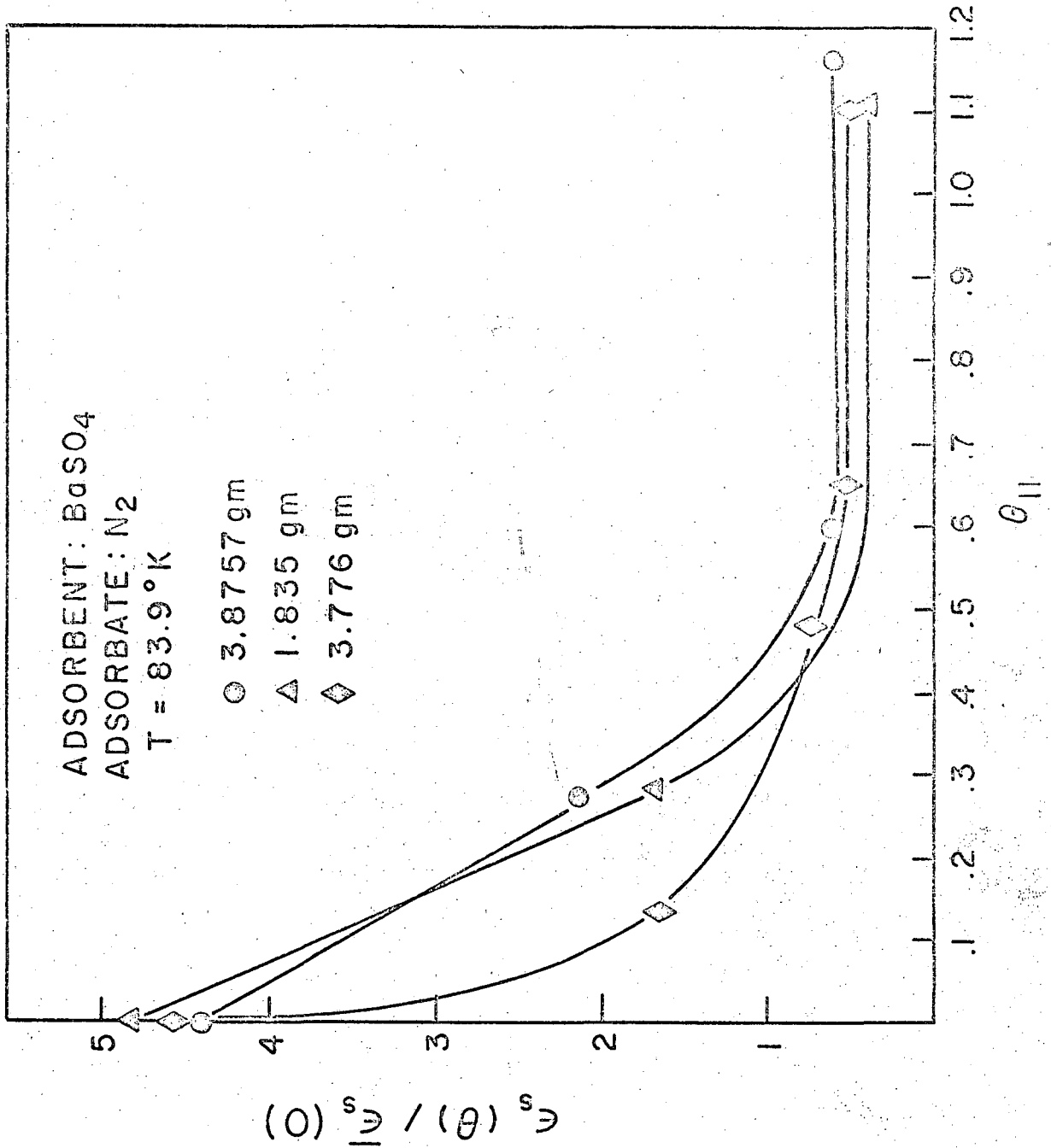


Fig. 8

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

