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I

THE EFFECT OF PREADSORBED STEARIC ACID ON THE ADSORPTIVE PROPERTIES OF TiO_2 (RUTILE): PART I

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ABSTRACT

Nitrogen adsorption isotherms on TiO_2 (rutile) coated with various amounts of stearic acid were determined, and the change in the net heat of adsorption of nitrogen integrated up to a monolayer was calculated as a function of the fraction of surface covered with acid. The orientation of the long chain fatty acid is believed to be parallel to the surface rather than perpendicular and experimental evidence for this fact is presented. After approximately 50% of surface coverage, the net heat of adsorption was found to be constant. This is in excellent agreement with the work of Steele and Aston. The magnitude of this change in the net heat of adsorption suggests a rather uniform distribution of energies on the surface of TiO_2. This fact and the fact that the surface area of TiO_2 did not change after coverage can be interpreted by the presence of sharp points and many sided sites on the surface of TiO_2 as postulated by Aston.

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INTRODUCTION

The adsorption potential for the adsorbate of a finely divided powder is known to decrease due to the presence of a preadsorbed material such as chemisorbed methanol or water.[1] The preadsorbate screens the surface ions, and this results in the lowering of the potential field emanating from the surface which reduces the force of attraction between the adsorbent and adsorbate. The additional effect of the preadsorbate on the surface area of the powder as measured by the B.E.T. equation has been reported by several workers;[2-4] the corresponding change in the B.E.T. C parameter, and hence in the net heat of adsorption (E_1-E_L) have also been reported, along with the change in the measured isosteric heat.[1]

If progressive amounts of a preadsorbate are added to the adsorbent up to the amount needed to completely cover the surface of the adsorbent with a monolayer of preadsorbate, the change in the measured net heat of adsorption (isosteric) integrated up to a monolayer can reveal interesting information on the extent of the surface heterogeneity and in some cases reveal the nature of this heterogeneity (cracks, sharp points, cavities, etc.). This approach has been attempted by Steele and Aston.[5] Results for the differential heat of adsorption of helium on a surface of

titanium dioxide (rutile) covered with increasing amounts of argon showed that after 6/10 of a monolayer of argon the differential heat of adsorption remained constant. Sixty percent of rutile is therefore energetically heterogeneous, the remaining sites being approximately of equal value.

Preliminary measurements by L. A. Girifalco[6] on the heat of wetting of fine powders as a function of preadsorbed long chain fatty acids indicated that they have a considerable effect on the heat evolved in the wetting process. Therefore, the progressive coating of the surface with a fatty acid followed by the adsorption of nitrogen at 77.5°K and 90.2°K should reveal interesting information on both the nature and extent of its heterogeneity. The orientation of these long chain fatty acid molecules, and the packing of these molecules on the surface of the powder when adsorbed from the vapor phase is also an interesting question which requires further experimental clarification. This is the first attempt to correlate the preadsorption of a long chain fatty acid and the subsequent adsorption of a gas with the heterogeneous nature of the adsorbent.

EXPERIMENTAL

Adsorbent: The adsorption measurements were made on TiO_2 (rutile) of reagent grade. The samples used assayed 99.45% in purity. The largest percentage of impurity was reported to be water soluble salts. The surface areas of the powders in the bare and coated conditions were calculated by use of the B.E.T. equation and equal to 6.66 m^2/gm with a precision of ±5%. TiO_2 is non-porous and hysteresis of the isotherm was not observed. The initial measurements on the bare powder were made after the powder had heated for one week at 600°C in an alumina crucible at atmospheric pressure. This procedure was found to be a sufficient surface preparation and the

results obtained were completely reproducible to within .7% which is within the experimental error of the amount adsorbed. However it does not remove all the irreversibly adsorbed water. Dawson[7] carried out experiments to determine the effect of degassing time on the adsorption capacity of rutile. In our study as in his the choice of degassing time was arbitrary. Since the bare powder was to be progressively coated with stearic acid, a systematic procedure prior to each preadsorption was adopted to insure that the remaining bare surface was in the same condition prior to the adsorption measurements which followed. This procedure will be outlined in a latter section of this paper.

Adsorbates: Nitrogen and helium, which was used for the dead space measurements, was of the highest commercial purity available (dry), and were further purified by the use of two cold traps which removed any impurities of a higher boiling point.

The preadsorbate was stearic acid ($C_{18}H_{36}O_2$) obtained from the Fisher Reagent Chemical Company. The area occupied by a stearic acid molecule in the perpendicular or parallel orientation is known;[8,9] it has a low melting point (69°C) which makes equilibration of the acid on the surface very convenient. The acid is in powder form and when melted forms a clear liquid which coats glass beads with a waxy film making it ideal for this work.* Its vapor pressure is very low at the temperatures of the adsorption measurements (77.5°K and 90.2°K); this makes the continuous coating and measurements of the same sample possible without risk of losing the stearic acid previously adsorbed. The fact that the sample could be used for

* The glass beads were used to transfer the stearic acid to the sample.

each increase in surface coverage, and not a new sample for each coverage, makes the objections of the research more meaningful. It is never possible to say that even powders from the same bottle which have received what appears to be the same preparation (degassing, heating, etc.) have the same surface characteristics; therefore the same sample should be used after each coating.

Since after each coating we are interested in the heats of adsorption from the bare part of the surface remaining and the combination (sample + stearic acid), the absolute magnitude of the heat of adsorption between the adsorbate and preadsorbate must not be known. This value should be zero (or very small), and within the limits of the Clausius-Clapeyron equation used to calculate this heat, the value for stearic acid-N_2 was found to be 0 ± 1 erg/cm^2. The reproducibility of these measurements was difficult. It is believed that a solutioning of the adsorbate occurred since a much longer time to attain the equilibrium pressure was observed. Furthermore, a systematic degassing procedure is difficult for stearic acid since at low pressures (10^{-6} mm Hg) it will vaporize. Degassing at low temperature (77.5°K or 90.2°K) will be ineffective.

APPARATUS

The adsorption measurements were performed with a standard volumetric apparatus. Pressure differences were read on a U-tube manometer by a precision cathetometer to ± 500 cm. The dead space was measured by the use of helium and agreed within .2%. The temperature of the bath was measured by a thermocouple (copper-constantan) and gas thermometer (nitrogen) by the equation of Dodge and Davis.[10] The temperature was found to be constant during the entire experiment and equal to 77.5°K for liquid

N_2 and 90.2°K for liquid O_2. The temperature must be constant to within ±.04°C to keep the relative error on the equilibrium pressure (as measured by the manometer) down to ±.2%. Boiling liquids maintained at a constant external pressure maintain their respective boiling point temperatures to within ±.004°C. The level of the liquid bath was maintained constant by a constant-level device. All pressures recorded below 3 mm Hg were corrected for thermal transpiration error by an equation due to Liang.[11]

PREPARATION OF POWDERS CONTAINING PREADSORBATE

Prior to each coating the sample which received the initial treatment is degassed for five hours at 10^{-7} mm Hg and 77.5°K. The sample cell under vacuum is then removed from the system and placed in a dry box. The dry box has an H_2-Ar atmosphere. A glass bead containing a known weight or preadsorbate is then placed on the powder which is shaken several times to insure that the bead is well surrounded by powder. The powder with the glass bead is then returned to the system and the He-Ar atmosphere removed by opening the cell to the static vacuum. The powder and bead are then degassed again for one hour at 10^{-4} mm Hg and 77.5°K, followed by one hour at static vacuum, at which time the vacuum is checked with the McLeod gauge. This was done to insure that no acid is evaporating and that no foreign gases adsorb on the TiO_2 prior to placing the powder in an oil bath for equilibration. At no time did the pressure increase. Equilibration is done under vacuum (10^{-1} mm Hg) to prevent any leakage into the cell from the atmosphere which would adsorb and change the surface. After from five to six days at 80°C ± 1°C, the oil bath is turned off; and the sample slowly cools to room temperature. The cell is then placed

on the system and held at 77.5°K for one hour to insure that any stearic acid still in the vapor phase adsorbs. The cold bath is then removed, and the sample is opened to the static vacuum of the system. The sample is then checked again to be sure that everything is exactly the same as conditions prior to the equilibration. The cold bath is then returned and the newly coated sample degassed for a few hours at 10^{-6} mm Hg. The adsorption measurement follows. This technique is tedious, but it was found to be completely successful.

FRACTION OF SURFACE COVERED WITH PREADSORBATE AND THE ORIENTATION OF THESE MOLECULES

Three assumptions can be made for the cross-sectional area per molecule of preadsorbate:

1. The molecule can be assumed to be standing upright with its carboxyl group at the surface. Each molecule then occupies an area equal to the area it would occupy in a close-packed film. The area is then 20.5 $Å^2$ per molecule.[8]

2. The major axis of the molecule could be parallel to the surface. The molecule would now occupy an area of 114 $Å^2$ per molecule.[9]

3. A mixture of the parallel and perpendicular orientation is also possible. The area occupied in this orientation is unknown.

The preliminary measurements by Girifalco who used a similar coating technique seems to indicate that the molecules are oriented "parallel" to the surface. His measurements were made by a precision calorimeter of high temperature sensitivity. Girifalco[6] performed measurements on the heat of wetting

$$\Delta H_{\omega} = \bar{\epsilon}_{SL} - \bar{\epsilon}_{S}(0)$$

where

$\bar{\epsilon}_{SL}$ = average energy of solid-liquid interface per cm^2

$\bar{\epsilon}_S(0)$ = total average energy of bare solid surface per cm^2

as a function of the amount of preadsorbed material for both lead chromate and aluminum oxide. Both stearic and perfluorodecanoic acid were preadsorbed on lead chromate. In the case of aluminum oxide, only one preadsorbate was used (stearic acid). The data obtained can be analyzed in the following way.

For stearic acid the perpendicular orientation results in a value of 2.31×10^{-4} mg of stearic acid per cm^2 of surface needed for monolayer coverage. The parallel orientation results in $.417\times10^{-4}$ mg per cm^2 of surface for complete coverage. As we progressively cover the bare surface with the preadsorbate, the heat of wetting will decrease. When coverage is complete, the heat of wetting should be a constant. This coverage will be assumed to correspond to the monolayer. The results obtained by Girifalco are shown in graphical form in Figs. 1, 2, 3, and 4. The scatter of the data is relatively large; and this, of course complicates any definite conclusions; however, an attempt will be made here to justify the parallel type of orientation. The error will be taken as the difference between the two measured heats of wetting at zero coverage as shown on the graphs.

In Fig. 1 we will draw three constant lines (I, II, and III). I is the upper extreme value, II the average value, and III the lower extreme value for the constant heat of wetting. $\theta_{\parallel}$ and $\theta_{\perp}$ correspond to monolayer coverage for the parallel and perpendicular orientation respectively.

Both the upper extreme and the average value imply that the long chain is parallel to the surface. However, the lower extreme implies that the perpendicular orientation is the more reasonable. Therefore, from these data alone no definite conclusion is possible. If the orientation is perpendicular, the adsorption of another fatty acid should result in the same value for the monolayer coverage since it is the carboxyl group which determines the area occupied by the fatty acid. Perfluorodecanoic acid ($C_9F_{19}COOH$) contains approximately half the number of carbon atoms as does stearic acid ($C_{17}H_{35}COOH$) and, hence, in the parallel orientation will cover about half as much area as stearic acid in the same orientation. We can use any one of the three constant lines as a reference for this comparison, but the average value (II) is the most reasonable and will be used. In Fig. 1 we see that a constant heat of wetting occurs at approximately $.85\times10^{-4}$ mg of stearic acid per cm^2 of $PbCrO_4$ and from Fig. 2 at 1.86×10^{-4} mg of perfluorodecanoic per cm^2 of $PbCrO_4$. The ratio of these two values is approximately 2. If the orientation of the two fatty acids were perpendicular, the ratio would be 1. Therefore, we conclude that within the precision and error of the heat of wetting data for $PbCrO_4$ that the preadsorbate is oriented parallel to the surface.

In Fig. 3 we see that all three constant lines imply that the orientation is parallel. The perpendicular orientation leads to too high a value ($\theta_\perp$) for all three constant lines; the data reach the constant values of the three lines significantly below 2.31×10^{-4} mg per cm^2. The average for all three is $.5\times10^{-4}$ mg stearic acid per cm^2 surface which compares quite well to $.417\times10^{-4}$ mg stearic acid per cm^2 surface for the parallel orientation.

Finally, Girifalco[6] found that heat of wetting curves for $PbCrO_4$ versus both stearic acid and perfluorodecanoic acid differed considerably. This method of calculation was such that the results should be independent. When the results are plotted assuming the parallel orientation, they do superimpose within the error of the experimental data. This is shown in Fig. 4.

In addition, the earlier theoretical work of De Boer[12] who presents some interesting considerations on the orientation of fatty acids on solid surfaces in terms of two dimensional condensation phenomena supports this conclusion. De Boer emphasizes that at low temperatures condensation in the perpendicular position is very difficult. The more recent theoretical contribution of Rubin[13] further strengthens the parallel orientation. However, it must be understood that the completely "parallel" orientation is a highly idealized condition. Entropy considerations would probably result in a sine wave type of coverage, that is, parts of the long chain molecule not in direct contact with the surface. This effect should decrease with increasing surface uniformity, that is, a smooth, even surface. At low coverage this idealized condition is more reasonable of course.

RESULTS AND DISCUSSION

Nitrogen Isotherms. Adsorption isotherms of N_2 on both bare and coated TiO_2 were determined at 77.5°K and 90.2°K. Typical results are shown in Fig. 5 and Fig. 6, where $\theta_\perp$ is the fraction of surface covered with preadsorbate calculated by assuming the perpendicular orientation; and $\theta_\parallel$ is the fraction of surface covered with preadsorbate assumed in the parallel orientation. The volume of gas adsorbed is easily calculated

from pressure measurements taken during the experiment by a mercury manometer. Equilibrium pressures were measured from 10 to 20 min after dosing the sample. The curves shown are examples of Type II, or sigmoid isotherms. The amount adsorbed at low pressures is large, followed by a linear portion where the rate of change in the amount adsorbed is small; and finally at the equilibrium vapor pressure the amount adsorbed approaches infinity; that is, condensation of the gas has occurred.

The data obtained gave consistent and smooth curves, indicating that the experimental procedure is satisfactory; that is, the data were completely reproducible within the error inherent in the measured parameters (pressure, volume, temperature). In Figs. 5 and 6 it is apparent that the preadsorbate (stearic acid) has caused a decrease in the amount of nitrogen physically adsorbed at any given pressure, and in particular, the "knee bend" in the vicinity of the monolayer is noticeably reduced. This reduction has its principal effect on the C parameter of the B.E.T. equation. A decrease in C is indicative of a lower "net heat" of adsorption, namely, the heat of adsorption of the first layer minus the heat of condensation ($E_1 - E_L$). It is apparent that the interaction of nitrogen with the combination substrate (TiO_2) and stearic acid is weaker than its interaction with the clean surface since the amount adsorbed after coverage is smaller. In general, the effect of the stearic acid on the isotherms is quite similar to that described by Holmes and Beebe.[1] This lowering of the isotherm has been reported by several workers.[1,3,4]

The isotherm data of Fig. 5 gave good straight lines when plotted using the linear form of the B.E.T. equation. Emmett[14] points out that the presence of a chemisorbed gas layer does not interfere with the measurement of the surface area of solids provided that there is no

blocking of the adsorbent's pores. There are, however, numerous indications in the literature that exceptions do exist.[15,16] The preadsorption of the large stearic acid molecule should change the surface area of fine powders which are either very porous or contain large numbers of macroscopic defects, such as cracks and cavities. Another possible reason for any diminution in surface area is a less condensed packing of the nitrogen molecules on the fatty acid surface. This is only a possibility when the preadsorbed acid creates a more heterogeneous surface which is rather unreasonable. Therefore, any decrease in the surface area of fine powders due to a physically preadsorbed layer is attributed to the blocking of large cavities which originally contributed to the surface area. This was demonstrated to be the case by Holmes and Beebe[1] who found that the thermal drift, or slow heat evolution, observed on a bare surface of bone mineral and attributed to narrow pores, was absent for the water-covered or methanol-covered surface. For the non-porous TiO_2, the preadsorption of the large stearic acid molecule seemed to have no effect on its surface area (within the accuracy of this value, ±5%) since the type of defects believed present on the surface do not make a significant contribution ($\leq$ 5%) to the surface area. The surface area of both bare and uncoated TiO_2 was found to be 6.66±.33.

HEATS OF ADSORPTION FOR TiO_2 - N_2 SYSTEM

The shape of the heat of adsorption curves for the TiO_2-N_2 system as a function of the number of moles adsorbed is well known to be a decreasing function as the number of moles adsorbed increases and is shown in Fig. 7. Kington and Aston[17] found that the differential heat of adsorption (ΔH_i) for the first increment of nitrogen admitted to the surface was about

5.2 $\frac{\text{Kcal}}{\text{mole}}$. The heat then showed a rapid decrease and reached a value of about 1.8 $\frac{\text{Kcal}}{\text{mole}}$ (ΔH_{n_m}) at the monolayer. Drain and Morrison[18] found the differential heat of adsorption (initial) to be about 6 $\frac{\text{Kcal}}{\text{mole}}$ and about 1.9 $\frac{\text{Kcal}}{\text{mole}}$ at the monolayer. A comparison between their results and that of this work is summarized in Table I.

Table I: Comparison Between the Heat of Adsorption Results for the TiO_2-N_2 System Between this Work and Other Workers

Workers	ΔH_i ($\frac{\text{Kcal}}{\text{mole}}$)	ΔH_{n_m} ($\frac{\text{Kcal}}{\text{mole}}$)
Kington and Ashton	5.2	1.8
Drain and Morrison	6.0	1.9
This work	5.0	1.7

The heats of adsorption were calculated from the adsorption isotherms (Figs. 5 and 6) by use of an equation of Clausius-Clapeyron type. The error on heats calculated by the use of this equation can be shown to be about ±15 $\frac{\text{cal}}{\text{mole}}$.[19] However, this should be looked upon as a lower limit. The points will usually have a larger scatter than ±15 $\frac{\text{cal}}{\text{mole}}$ around the smooth curve connecting each point up to a monolayer coverage and above. In the pressure range of the measurements made, a scatter of ±50 $\frac{\text{cal}}{\text{mole}}$ is believed to be a reasonable error. It would be interesting to compare these experimental ΔH_i's to a theoretical calculation which would include all the important forces between adsorbed molecules and the adsorbent surface (dispersion, polarization, etc.). However, the occurrence of corners, edges and irregularities makes such an ideal approach strictly incorrect. Drain and Morrison[20] point out that roughly 10% of the surface

atoms are at edges and corners. There are, in addition, several crystal faces possible. The (110) and (100) are those planes for which cleavage is possible[21] and are believed to be the most dominant for rutile in powder form.[7] The electrostatic contribution to the heat of adsorption should be quite large in the case of TiO_2. This fact has been verified by the careful work of Morrison and Drain[18] which led them to the conclusion that the nonuniformity in the observed heat of adsorption of TiO_2 is a result of the heterogeneity of electrical forces rather than of dispersion forces. Any change then in the heat of adsorption with a preadsorbed fatty acid is due to the dielectric property of the acid which will lower the magnitude of the electric field emanating from the surface.

It is suggested here then that the observed change in the heat of adsorption as a function of the preadsorbed acid is caused by a lowering of the electric field gradient. This will reduce the force of attraction between the surface and the adsorbate and, hence, result in a lower heat of adsorption. Measurements were made on the heat of adsorption of N_2 on a bare TiO_2 surface, on TiO_2 plus .19 layer of stearic acid, .51 layer and .71 layer. The preadsorption of .19 layer of stearic acid reduces the heterogeneity of the surface and removes sites with heats of 3.78 $\frac{\text{Kcal}}{\text{mole}}$ or greater (Fig. 7). At .51 layer a small change is observed, and only sites with heats of 3.53 $\frac{\text{Kcal}}{\text{mole}}$ or less are left. No change was observed with additional stearic acid coverage. The shape of the curves remains the same. This change of 1.51 $\frac{\text{Kcal}}{\text{mole}}$ is independent of lateral interactions since initially they can be neglected. Steele and Aston[5] performed a similar experiment on the heat of adsorption of He on TiO_2 covered with various amounts of argon up to a monolayer. It was found that after

.60 of a monolayer of argon the differential heat of adsorption remained unchanged with coverage. This value compares well with the .51 value observed in this study. Steele and Aston[5] conclude that the heat of adsorption at very low coverages is due to many-sided sites (that is, microscopic defects) which make a negligible contribution to surface area. This is in agreement with the fact that the surface area of TiO_2 does not change with preadsorbed stearic acid. The presence of many-sided sites will definitely influence the surface field gradient and hence the force of attraction between the surface and the bulk gas. Therefore, the conclusion of Drain and Morrison[18] does not conflict with that of Steele and Aston.[5] Indeed, they complement each other.

The total or net integral experimental heats calculated up to a monolayer ($\bar{Q}$) are tabulated in Table II as a function of the fraction of surface covered with the preadsorbate for both the perpendicular and parallel orientation, $\theta_{\perp}$, $\theta_{\parallel}$. The heats $\bar{Q}_{B.E.T.}$ calculated from the constant C of the B.E.T. equation are also reported. The fact that 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[22] mentions that the B.E.T. heats can be even smaller than 50% of the measured value.

This total heat of adsorption up to the monolayer 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. The sum of the lateral interactions will be taken to be approximately equal to the heat of condensation. This is of course an upper limit to its value, but for the TiO_2-N_2 system

Table II: Summary of Data for TiO_2, N_2 Gas

$\bar{Q}$ $(\frac{ergs}{cm^2})$	$\bar{Q}_{B.E.T.}$ $(\frac{ergs}{cm^2})$	E_N $(\frac{ergs}{cm^2})$	$\theta_\perp$	$\theta_\parallel$
53.80	25.28	28.52	0%	0%
36.53	25.28	11.25	3.5%	18.9%
26.91	19.32	7.59	9.5%	51.3%
26.91	19.32	7.59	13.0%	71.3%

this is a reasonable choice (Table I). Therefore, the total measured net heat of adsorption [total heat (experimental) - heat of condensation], $\bar{Q}$ is equal to the net heat of adsorption on the homogeneous part of the surface as calculated by the B.E.T. constant $C(\bar{Q}_{B.E.T.})$ plus the net heat due to the heterogeneity (E_N) 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 or even zero. This will, of course, depend on the effectiveness of the preadsorbate and on the nature of the surface. Both $\bar{Q}$ and $\bar{Q}_{B.E.T.}$ are plotted versus $\theta_\parallel$ in Fig. 8. Obviously, the change of $\bar{Q}$ with $\theta_\parallel$ is related to the distribution of energy on the surface. A method based on the earlier theoretical work of Girifalco[23] has been developed by which the distribution of surface energies with respect to the average surface energy of the bare powder can be obtained from a knowledge of this variation of $\bar{Q}$ with the fraction of the surface covered with acid. This method will be presented in a later paper, and will be applied to the data obtained on the TiO_2-N_2 system and to the $BaSO_4$-N_2 system as well.

CONCLUSIONS

The decrease in the net heat of adsorption as a function of the fraction of the surface covered with stearic acid in the parallel orientation (Fig. 8) suggests that the adsorption energy is distributed over a large fraction of the surface. Honig and Reyerson[24] in a study of the adsorption of oxygen, argon and nitrogen on rutile found that the distribution of adsorption energies for nitrogen was very nearly uniform over a large range of energy values also. The fact that the contribution from the surface heterogeneity is not eliminated strengthens the conclusion of Drain and Morrison[18] regarding the nonuniformity of TiO_2 as the result of the heterogeneity in electrical forces. A fatty acid should be moderately successful in eliminating any nonuniformity caused by large cavities, but could only reduce a nonuniformity caused by heterogeneous electrical forces on the surface. In the case of the TiO_2 surface the observed heterogeneity is probably due to differing electrostatic forces on the surface which are caused by the presence of sharp points and many sided sites as postulated by Aston et al.[25] Such defects make a negligible contribution to the total surface area, and this is the reason for the fact that the surface area of TiO_2 was indeed constant with coverage.

Finally, the fact that the observed heat of adsorption remained constant after approximately 50% coverage is in good agreement with that of Steele and Aston,[5] and therefore it seems that 50% of the surface of TiO_2 is heterogeneous. The relative distribution of energy in this heterogeneous region will be the subject of a later paper.

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REFERENCES

1. J. M. Holmes and R. A. Beebe, Solid Surfaces and the Gas-Solid Interface, in Advances in Chemistry, Vol. 33, (American Chemical Society, Washington, D.C., 1961).

2. A. V. Kiselev, N. V. Kovaleva, A. Ya. Korolev, and K. D. Shcherbakova, Compt. rend. Acad. Sci. URSS (Dokl. Akad. Nauk SSSR) 124, 617 (1959).

3. D. S. McIver and H. H. Tobin, J. Phys. Chem. 64, 683 (1960).

4. F. S. Stone and P. F. Tiley, Nature 167, 654 (1951).

5. W. A. Steele and J. G. Aston, J. Amer. Chem. Soc., 79, 2393 (1957).

6. L. A. Girifalco, Ph.D. Thesis, University of Cincinnati, (1954).

7. P. T. Dawson, J. Phys. Chem., 71, 838 (1967).

8. J. J. Bikerman, Surface Chemistry for Industrial Research, (Academic Press, Inc., New York, 1948), Chapter V.

9. E. H. M. Wright, J. Chem. Soc., 2267 (1964).

10. B. Dodge and H. Davis, J. Amer. Chem. Soc., 49, 610 (1927).

11. S. C. Liang, J. Appl. Phys., 22, 148 (1951).

12. J. H. De Boer, The Dynamical Character of Adsorption, (Oxford Clarendon Press, 1953).

13. R. J. Rubin, J. Chem. Phys. 43, 2392 (1965).

14. P. H. Emmett, Catalysis, Vol. I., P. H. Emmett, Ed., (Reinhold Publishing Corp., New York, 1954) p. 51.

15. S. T. Teichner and J. A. Morrison, Trans. Faraday Soc., 51, 961 (1955).

16. M. V. C. Sastri, T. S. Viswanathan, and T. S. Nagayunan, J. Phys. Chem., 63, 518 (1959).

17. G. L. Kington and J. G. Aston, J. Amer. Chem. Soc., 75, 1929 (1951).

18. L. E. Drain and J. A. Morrison, Trans. Faraday Soc., 49, 654 (1953).

19. S. Ross and J. P. Olivier, On Physical Adsorption, (Interscience Publ., New York, 1964).

20. L. E. Drain and J. A. Morrison, Trans. Faraday Soc., 48, 316 (1952).

21. J. D. Dana, The System of Minerology, 7th Ed., (Chapman and Hall Ltd., London, 1944), p. 554.

22. S. Brunauer, Solid Surfaces and Gas-Solid Interface, in Advances in Chemistry, Vol. 33,(American Chemical Society, Washington, D. C., 1961), p. 7.

23. L. A. Girifalco and R. J. Good, J. Phys. Chem., 61, 904 (1957).

24. J. M. Honig and L. H. Reyerson, J. Phys. Chem., 56, 140 (1952).

25. J. G. Aston, E. J. Tomezsko, and H. Chon, Solid Surfaces and the Gas-Solid Interface, in Advances in Chemistry, Vol. 33, (American Chemical Society, Washington, D. C. , 1961).

FIGURE CAPTIONS

Fig. 1 The heat of wetting of lead chromate as a function of preadsorbed stearic acid.

Fig. 2 The heat of wetting of lead chromate as a function of the amount of preadsorbed perfluorodecanoic acid.

Fig. 3 The heat of wetting of aluminum oxide as a function of the amount of preadsorbed stearic acid.

Fig. 4 Heat of wetting of lead chromate as a function of preadsorbed perfluorodecanoic acid and stearic acid in the parallel orientation.

Fig. 5 Adsorption isotherm of nitrogen with the fraction of the preadsorbed stearic acid as parameter at 77.5°K.

Fig. 6 Adsorption isotherms of nitrogen with the fraction of the preadsorbed stearic acid as parameter at 90.2°K.

Fig. 7 Isosteric heat of adsorption of nitrogen versus moles adsorbed with the fraction of the surface covered with stearic acid as parameter.

ΔH_S - heat of condensation

N_M - monolayer coverage

Fig. 8 The net experimental heat and the net B.E.T. heat as a function of $\theta_{\parallel}$ for TiO_2.

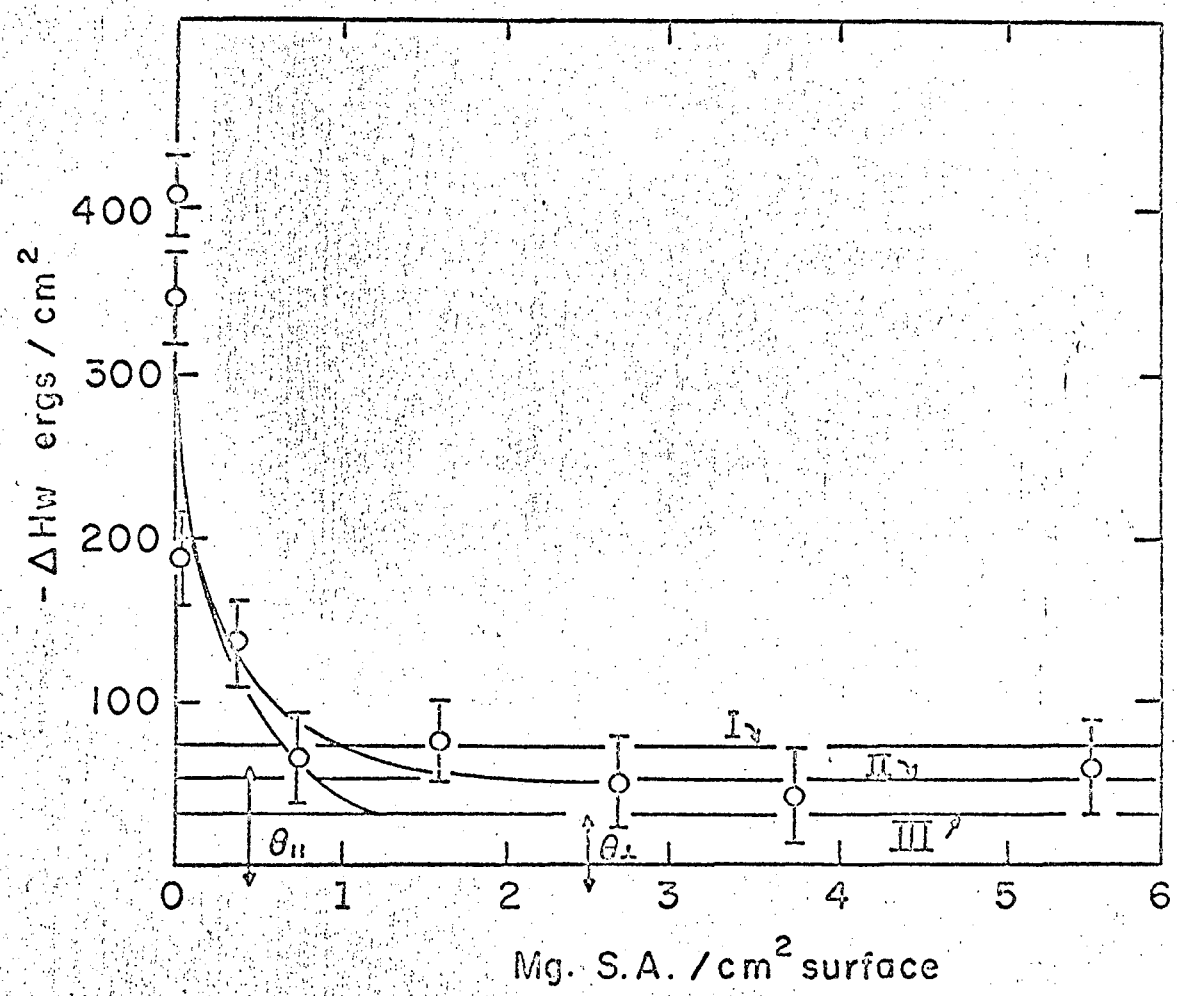
400
300
200
100
- ΔHw ergs / cm²
0
1
2
3
4
5
6
Mg. S.A. / cm² surface
I
II
III
θ∥
θ⊥

Fig. 1

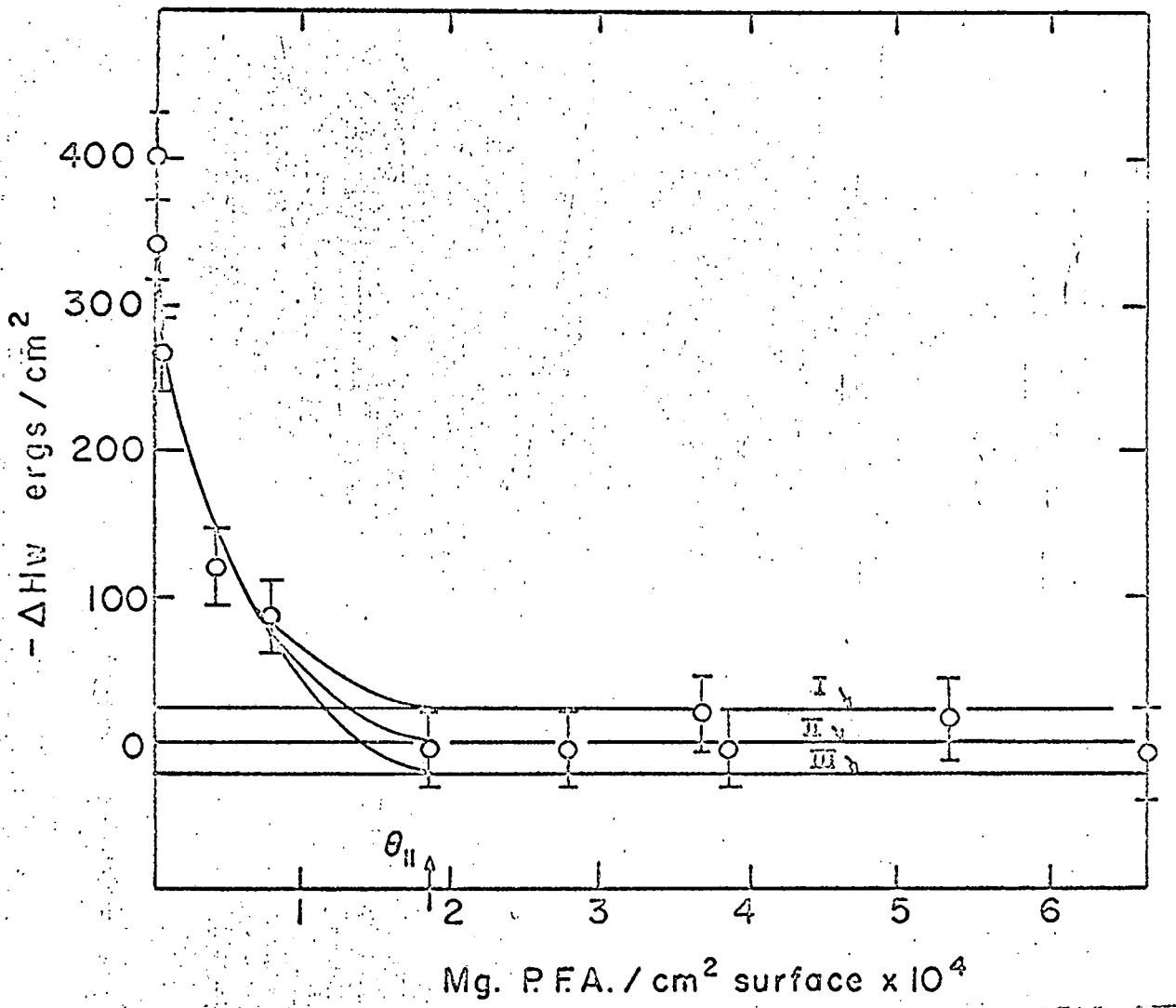
400
300
200
100
0
- ΔHw ergs / cm²
I
II
III
θII
1
2
3
4
5
6
Mg. P.F.A. / cm² surface x 10⁴

Fig. 2

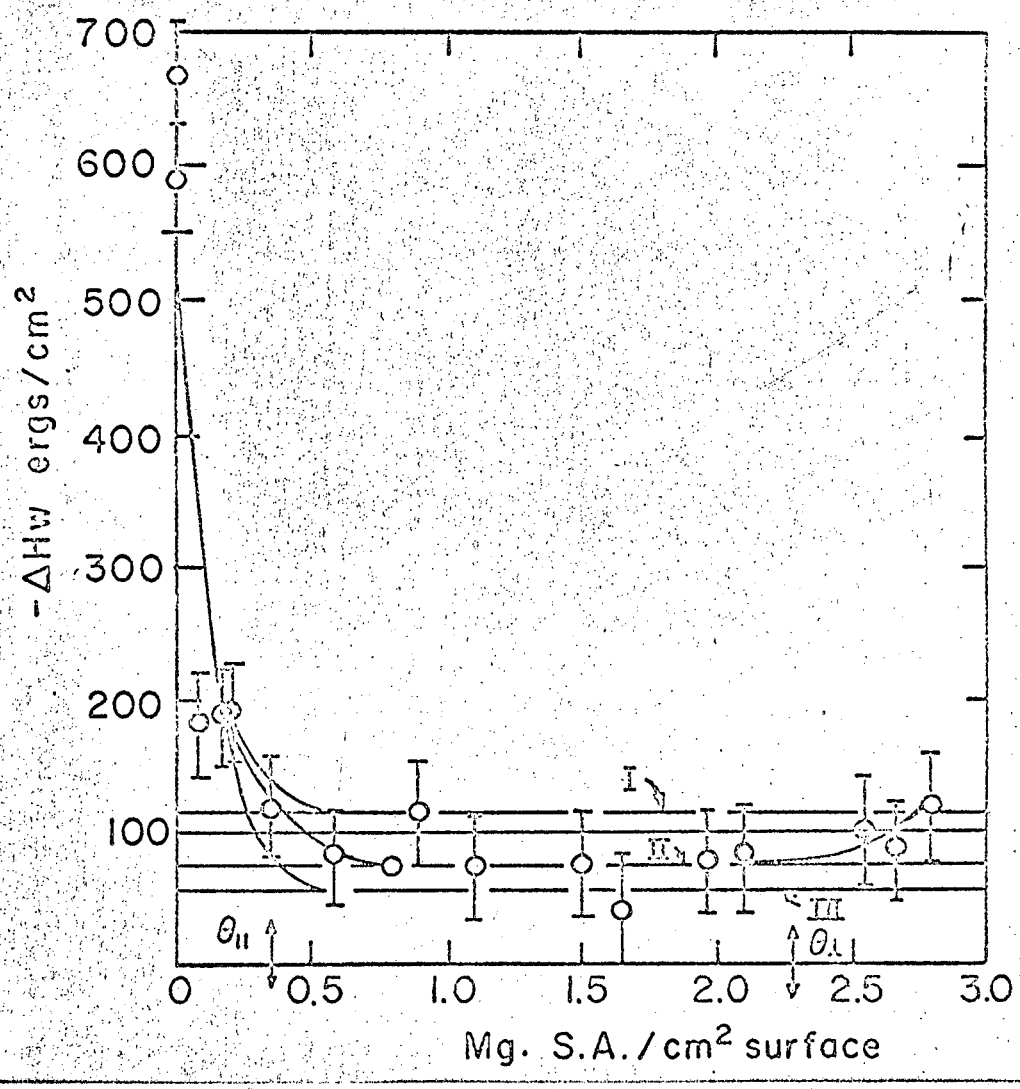
700
600
500
400
300
200
100
-ΔHw ergs/cm²
I
II
III
θ∥
θ⊥
0
0.5
1.0
1.5
2.0
2.5
3.0
Mg. S.A./cm² surface

Fig. 3

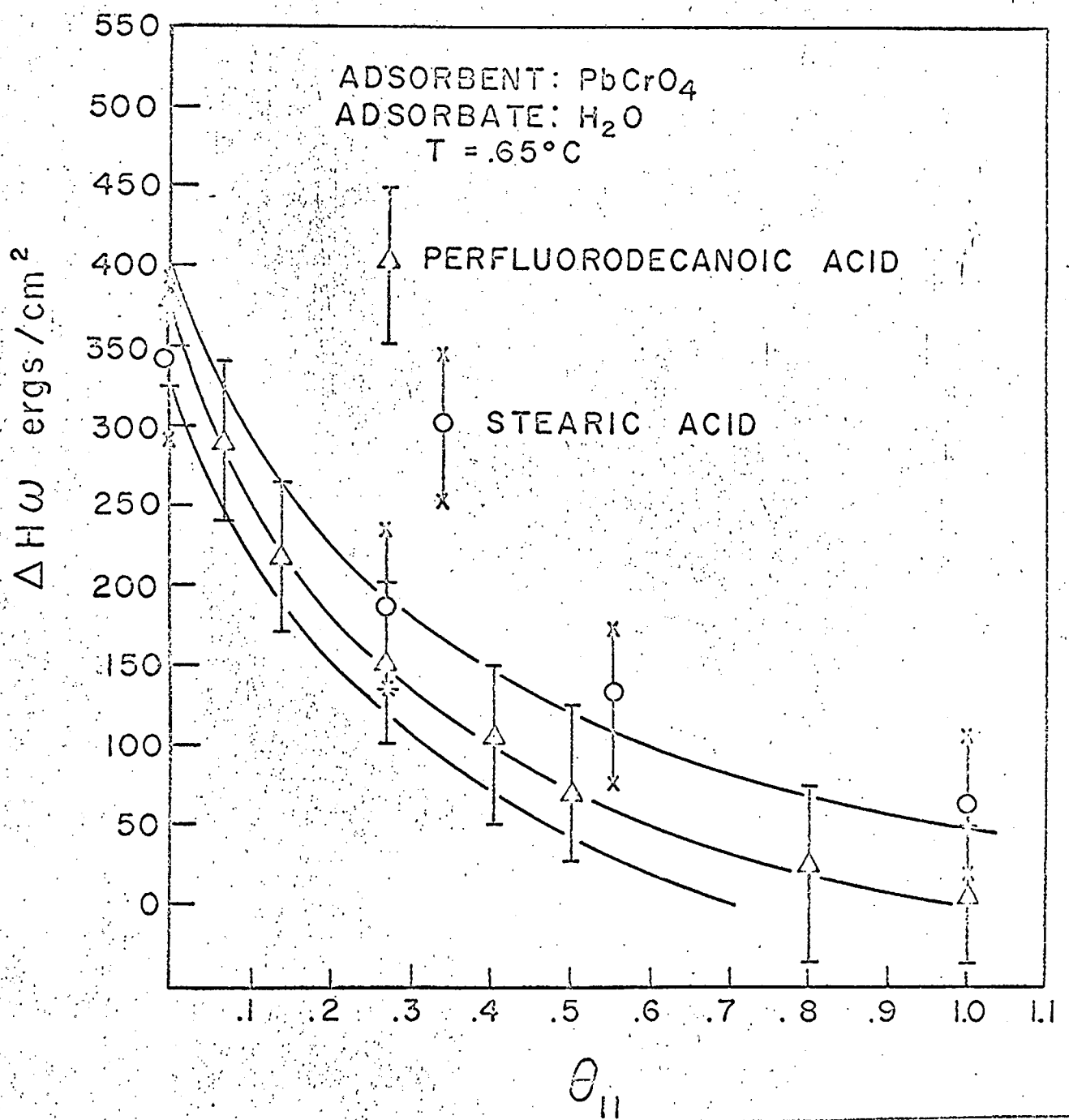
ADSORBENT: $PbCrO_4$
ADSORBATE: H_2O
T = .65°C
PERFLUORODECANOIC ACID
STEARIC ACID
$\Delta H\omega$ ergs/cm^2
550
500
450
400
350
300
250
200
150
100
50
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
θ_{11}

Fig. 4

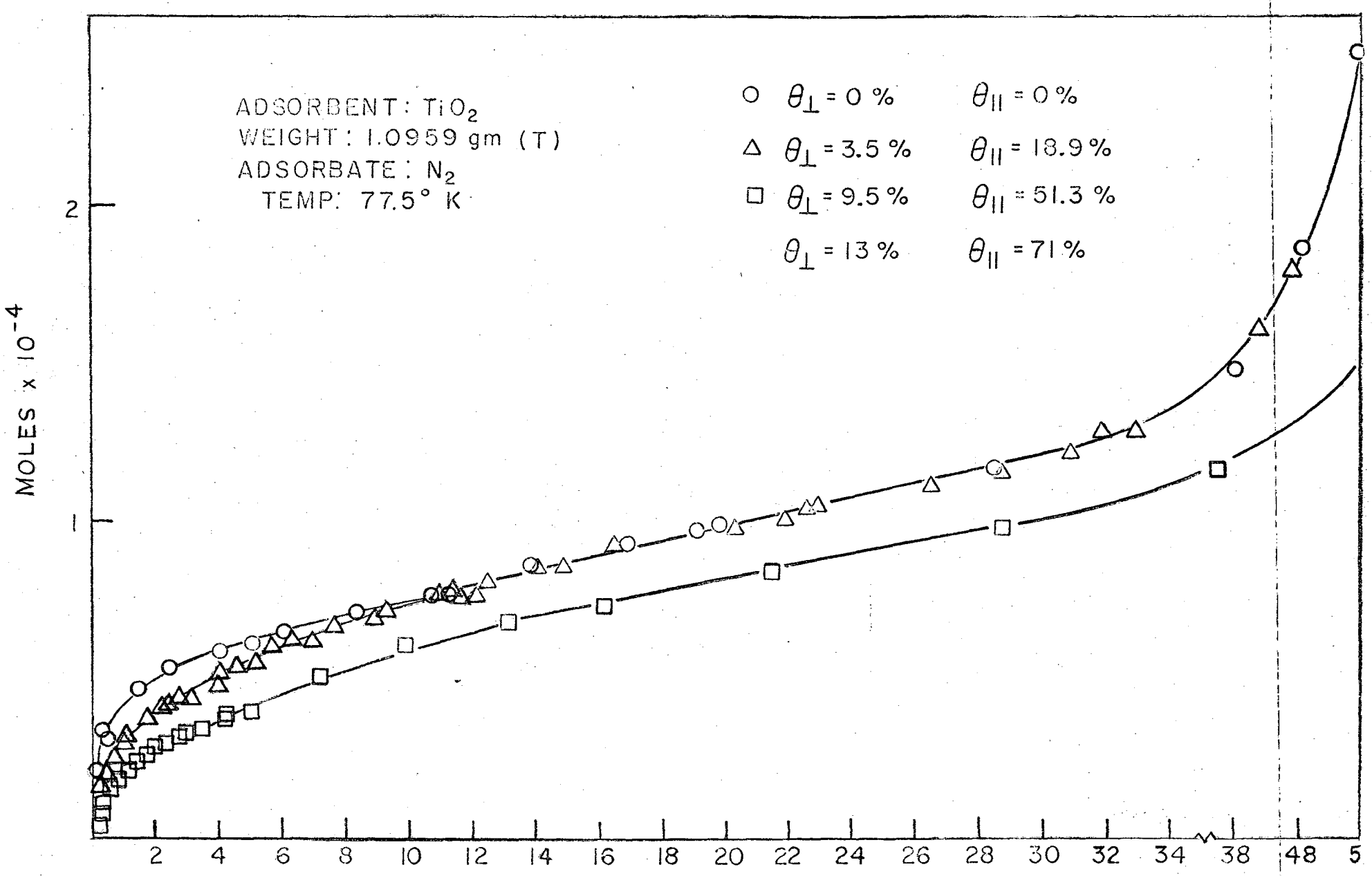
ADSORBENT: TiO_2
WEIGHT: 1.0959 gm (T)
ADSORBATE: N_2
TEMP: 77.5° K
○ $\theta_\perp$ = 0 % $\theta_{||}$ = 0 %
△ $\theta_\perp$ = 3.5 % $\theta_{||}$ = 18.9 %
□ $\theta_\perp$ = 9.5 % $\theta_{||}$ = 51.3 %
$\theta_\perp$ = 13 % $\theta_{||}$ = 71 %
MOLES x 10^{-4}
2
1
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 38 48 5
P_i' (cm) Hg

Fig. 5

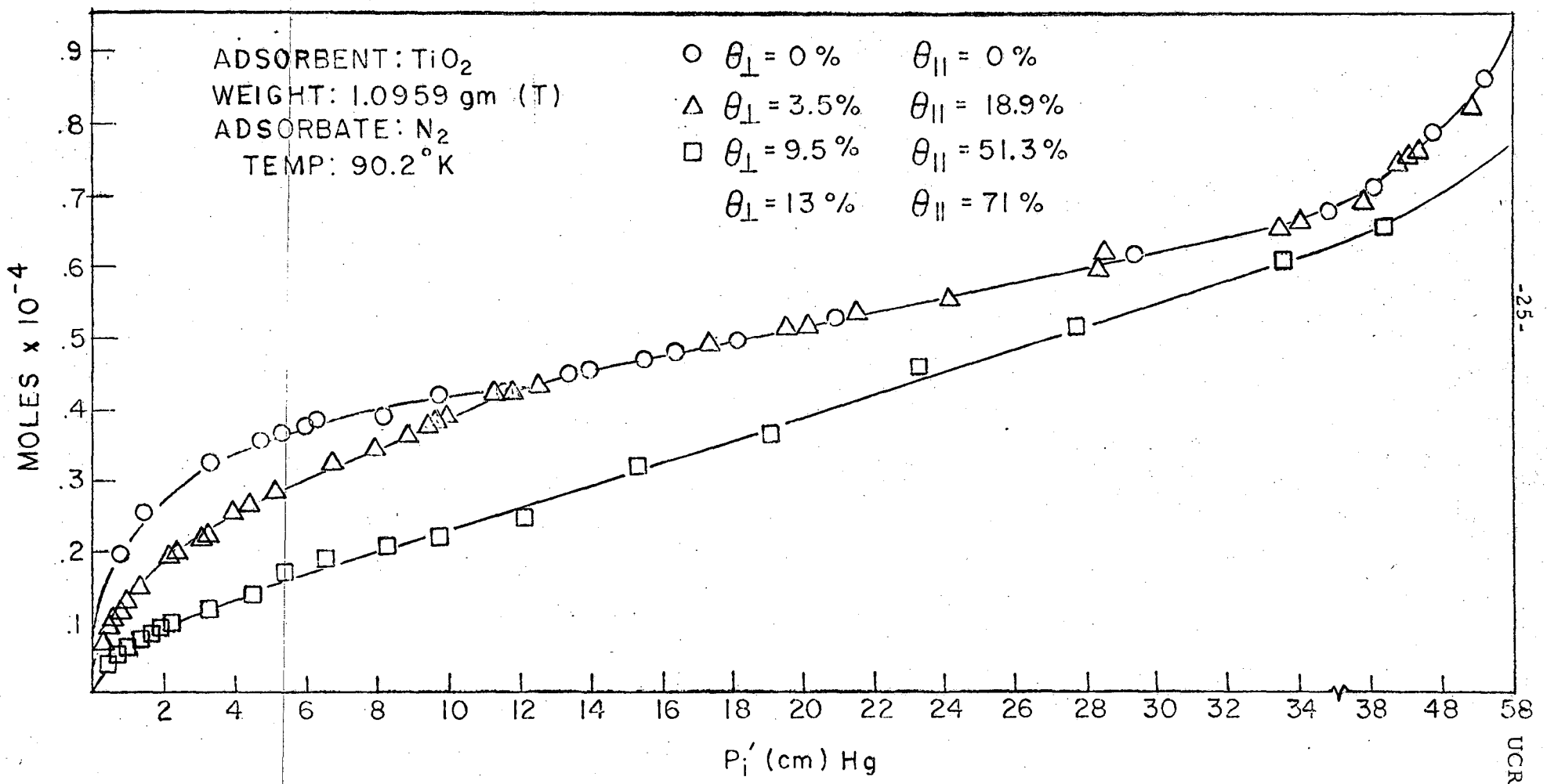
ADSORBENT: TiO_2
WEIGHT: 1.0959 gm (T)
ADSORBATE: N_2
TEMP: 90.2°K
○ $\theta_\perp$ = 0 % $\theta_{||}$ = 0 %
△ $\theta_\perp$ = 3.5% $\theta_{||}$ = 18.9%
□ $\theta_\perp$ = 9.5 % $\theta_{||}$ = 51.3%
$\theta_\perp$ = 13 % $\theta_{||}$ = 71 %
MOLES x 10^{-4}
.9
.8
.7
.6
.5
.4
.3
.2
.1
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 38 48 58
P_i' (cm) Hg

Fig. 6

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