Title

THEORETICAL DESCRIPTION OF THE RELATIVE DISTRIBUTION OF ENERGY ON A SOLID SURFACE AND ITS APPLICATION TO TiO2= PART II

Permalink

https://escholarship.org/uc/item/63s1m5c7

Authors

Morabito, J.M.
Duty, P.F.

Publication Date

1968-04-01

UCRL-17834

cy 2

University of California

Ernest O. Lawrence Radiation Laboratory

THEORETICAL DESCRIPTION OF THE RELATIVE DISTRIBUTION OF ENERGY ON A SOLID SURFACE AND ITS APPLICATION TO TiO_2: PART II

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

April 1968

Submitted to: J. Phys. Chem.

UCRL-17834
Preprint

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

THEORETICAL DESCRIPTION OF THE RELATIVE DISTRIBUTION OF ENERGY ON A SOLID SURFACE AND ITS APPLICATION TO TiO_2: PART II

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

April 1968

THEORETICAL DESCRIPTION OF THE RELATIVE DISTRIBUTION OF ENERGY ON A SOLID SURFACE AND ITS APPLICATION TO TiO_2: PART II.

J. M. Morabito, Jr.[†]
University of Pennsylvania, Philadelphia, Pa.,

and

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

ABSTRACT

A method has been developed by which the relative distribution of energy on a solid surface could be measured by a technique free of complicating models, experimental difficulties, and intractable equations. The necessary equations are derived, and the assumptions upon which they rest are carefully analyzed. They do not include arbitrary parameters, and only one constant which depends on the gas adsorbed must be calculated.

When applied to data on TiO_2 it was found that approximately 10% of its surface had energies two times greater than the average surface energy ($\bar{\epsilon}_S(0)$). 50% of its surface was homogeneous in energy, and equal to approximately half of the average surface energy.

[†] Present Affiliation: Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California

I. INTRODUCTION

A detailed adsorption study can give considerable insight into the energy, activity and physiochemical structure of solid surfaces; and is of interest since it combines many aspects of surface phenomena into a well defined thermodynamic system.

Real surfaces possess flaws which result in a surface heterogeneity and the occurrence of various adsorption energies. The distribution of these energies and the underlying nature of this surface heterogeneity is a complex problem. Previous attempts[1,2] to theoretically calculate this distribution function have resulted in complex equations, not only difficult to solve,[3] but of little use in the treatment of thermodynamic data. Therefore, the primary objective of this paper is to develop a theoretical description of the relative distribution of energy on a solid surface which is straight forward, easy to use, and unique in its approach. The thermodynamic description of adsorption phenomena together with fundamental equations from the theory of adhesion, and of a method developed by L. A. Girifalco[4] relating the energy of adhesion and cohesion of two phases will enable us to derive the necessary equations. These equations relate the surface energy with respect to the average surface energy of the total bare solid ($\bar{\epsilon}_S(0)$) to three parameters ($Q(\Theta)$, Θ, $2\epsilon_L$). $2\epsilon_L$, the surface energy of a thin (monoatomic) film is a constant and depends only on the gas used in the adsorption measurements (nitrogen, oxygen, etc.). It can be calculated (approximately) by the use of Lennard-Jones potentials. The other two, the net heat of adsorption $\bar{Q}(\Theta)$ and the fraction of the surface covered (Θ) with a long chain fatty acid, are easily measured.[5] All simplifying assumptions are carefully explained with respect to their validity and its effect on the results.

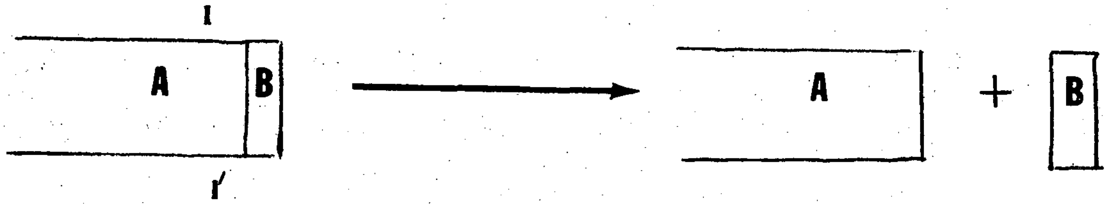
A theory of surface energies has not resulted from this study; but rather, through a useful application of well defined thermodynamic concepts, a valid approach was successfully developed (which will increase our understanding of the effect of surface heterogeneity on the relative distribution of energy present on the surface.

II. FUNDAMENTALS OF ADHESION

This development is based on earlier work by Girifalco[4] who attempted to obtain energies of adhesion and cohesion from heat of wetting and adsorption data using an approximate theory based on Fowler and Guggenheim integrals.[6] His theory was derived for bulk phases, but it is applicable to the energy of adhesion between solids and thin films also if the surface energy of the thin film is known or can be calculated.

The following definitions of the thermodynamic functions of adhesion are similar to those for bulk phases.[7]

Adhesive failure between a solid and a thin film can be represented as follows:



where II' is the interface between the solid and thin film which is destroyed as shown. The two separated phases have a surface energy defined below:

ϵ_A = surface energy of A per cm^2. (Bulk Phase)

E_B = "surface energy" of B per cm^2. (Thin Film)

ϵ_{AB} = interfacial energy of $\frac{A}{B}$ interface per cm^2.

The difference in energy between $(\epsilon_A + E_B)$ and ϵ_{AB} is the energy of adhesive failure and will be defined as ΔE^a_{AB}. The energy of adhesion is $-\Delta E^a_{AB}$.

$$\Delta E^a_{AB} = \epsilon_A + E_B - \epsilon_{AB} \tag{1}$$

Similar equations can be written for the free energy of adhesive failure, ΔF^{a}_{AB}, and the entropy of adhesive failure, ΔS^{a}_{AB}. If both phases are the same, the process is that of cohesive failure. The energy of cohesive failure for phase A is

$$\Delta E^{C}_{a} = 2\epsilon_{A} \tag{2}$$

and for phase B:

$$\Delta E^{C}_{B} = 2\epsilon_{B} \approx E_{B} \tag{3}$$

The energy of cohesion for a <u>monoatomic</u> film is equal to its surface energy. $2\epsilon_B$ is used in analogy to Eq. (2) for phase A.

The energy of adhesion for the solid-thin film system can be obtained from the heat of adsorption up to a <u>monolayer</u> and $2\epsilon_B$. Before the calculation for $2\epsilon_B$ is shown, the relation between the energy of adhesion and adsorption will be given. The two-phase adhesive system is formed by adsorption from the vapor state, and it can be represented as follows:

1. Condense the vapor to the adsorbed phase.
2. Extend the adsorbed phase into a film of the same area as the substrate.
3. Adhere the film to the substrate.

The net energy change is the heat of adsorption ΔH_m (isosteric) - the isosteric heat integrated to one monolayer. The reverse process is schematically shown in Fig. 1. In terms of the three steps of Fig. 1

$$- \Delta H_{m} = \Delta E^{\alpha}_{AB}\Sigma - (2\epsilon_{B})\Sigma + \Delta H_{v} \tag{4}$$

for the actual process of adsorption

$$+ \Delta H_{m} = - \Delta E^{\alpha}_{AB}\Sigma + (2\epsilon_{B})\Sigma + \Delta H_{s} \quad . \tag{5}$$

The PΔV terms in steps 2 and 3 are negligible.

ΔH_v = heat of vaporization of the bulk liquid to the vapor

ΔH_s = heat of condensation of the vapor to the bulk liquid drop

$2\epsilon_B$ = surface energy of phase B (thin film)

ΔE^{α}_{AB} = energy of adhesion of phase B to the substrate A

Σ = surface area of the substrate

Solving for ΔE^{α}_{AB}

$$-\frac{(\Delta H_m - \Delta H_s)}{\Sigma} + 2\epsilon_B = \Delta E^{\alpha}_{AB} \,. \qquad (6)$$

define $-\dfrac{(\Delta H_m - \Delta H_s)}{\Sigma}$ as $-\bar{Q}(\Theta)$ $\quad -\bar{Q}(\Theta) + 2\epsilon_B = \Delta E^{\alpha}_{AB}$ (7)

The quantity $(\Delta H_m - \Delta H_s)$ is the "net" heat of adsorption up to a monolayer coverage.[5]

III THE Φ CONSTANT

A surface atom or molecule is in a different energy state than that of an atom or molecule inside the solid. This energy difference is called the surface total energy or surface energy. Not only is the energy of a surface atom (or molecule) greater, but the free energy of the atom is also greater. This excess free energy is the reason for the "activity" of the surface. Theoretical calculations based on ideal crystals[8,9] at $T = 0^\circ K$ and for surfaces at $T > 0^\circ K$[10] have given only order of magnitude accuracy. There is still much to be done; and any advance in this area is highly desirable, even if only approximate answers result. One such theory suitable for this objective is that of Girifalco and Good.[11,12] The part of their theory useful for our purposes will be restated here for the convenience of the reader.

The Berthelot[13] relation gives the relationship between the attractive constants in the intermolecular potential functions of like molecules A_{AA} and A_{BB} and unlike A_{AB} as

$$\frac{A_{AB}}{(A_{AA}\ A_{BB})^{1/2}} = 1. \tag{8}$$

By analogy we can take a similar ratio involving the energies (or free energies of adhesive failure (ΔE^{α}_{AB}, ΔF^{α}_{AB}) and cohesive failure (ΔE^{C}_{A}, ΔF^{C}_{A} or ΔE^{C}_{B}, ΔF^{C}_{B}). The result for the energy is

$$\frac{E^{\alpha}_{AB}}{(\Delta E^{C}_{A}\ \Delta E^{C}_{B})^{1/2}} = \Phi \quad . \tag{9}$$

Girifalco[4] was able to derive the following expression for Φ

$$\Phi = \frac{A_{AB}}{(A_{AA}\ A_{AB})^{1/2}} \quad \frac{r_{o_{AA}}^{2}\ r_{o_{BB}}^{2}}{r_{o_{AB}}^{4}} \tag{10}$$

where $r_{o_{AA}}$, $r_{o_{BB}}$, and $r_{o_{AB}}$ are the equilibrium distances of separation between molecules and unlike respectively. In order to evaluate Φ, the constants (A_{AB}, A_{AA}, and A_{BB}) in the potential energy function and the equilibrium distances must be known. These are known only for the simplest systems. If the two phases have similar potential functions, then it is a good assumption to say $A_{AB} = (A_{AA}\ A_{BB})^{1/2}$. In addition, if the molecules have similar geometry, the ratio of equilibrium distances can be replaced by

$${\frac{4V_A^{*\frac{1}{3}}\ V_B^{*\frac{1}{3}}}{\left(V_A^{*\frac{1}{3}} + V_B^{*\frac{1}{3}}\right)}}^{12} , \tag{11}$$

where V_A^* and V_B^* are the molar volumes of the two phases.

Φ is, therefore, equal to 1 for similar phases; and it deviates from 1 (higher or lower) when the interactions between the two phases (ΔE_{AB}^{α}) are higher or lower than $(\Delta E_A^C\ \Delta E_B^C)^{1/2}$. The limitations of the approach are discussed in considerable detail by Girifalco in reference 4.

We will make use only of the basic definition of Φ and Eqs. (2,3,9)

$$\Phi = \frac{\Delta E_{AB}^{\alpha}}{(4\epsilon_A \epsilon_B)^{1/2}} \tag{12}$$

We will make no attempt to calculate the absolute value of Φ. For a polar solid and a non-polar liquid it has been shown[12] that Φ is less than 1.

The main purpose of the above presentation is to carefully define Φ. As stated, it is merely the ratio between three well defined parameters, one of which (ΔE_{AB}^{α}) can be measured experimentally by an adsorption technique; the other two are known from other measurements or theoretical calculations. When phase A is a solid, ΔE_S^C of Eq. (9) is not well known and does vary over a wide range for the particular state of the solid (powder, single crystal) and history (thermal treatment, etc.). If the second phase is liquid, ΔE_L^C is well known for the bulk phase and can be calculated for the thin liquid film as shown in the next section. How we will use the definition of Φ and heat of adsorption data as a function of some preadsorbed molecule will be shown in Section V.

IV CALCULATION OF THE SURFACE ENERGY OF A THIN FILM

Aggregations of atoms or molecules in a liquid or solid are due to attractive interactions. Since the attractive force-distance relationships are well known for the relatively simple molecules, we will make use of them to calculate the surface energy of a thin film of liquid nitrogen and oxygen. Together with this attraction is a repulsive term, and the balance of interparticle attractions and repulsions will govern the structure and constitution of the phase at the absolute zero of temperature. At $T > 0°K$ thermal energy will cause random vibrational, rotational, and translational motion and must be corrected for when using potential functions which describe the variation in energy of an atom or molecule solely from changes in its distance from another particle. The potential used for nitrogen is that reported in reference 14.

We will use a thermodynamic cycle to calculate the surface energy as shown in Fig. 2.

In (a) we take the thin film at $T = 77.5°K$ and 1 atm to the gas phase. The enthalpy needed for this process is given by

$$\Delta H_c = \Delta H_o + \int_{0°K}^{77.5°K} \Delta C_p \, dT. \qquad (13)$$

ΔH_o is the enthalpy or internal energy* of the film at the absolute zero of temperature. ΔC_p is the difference in the heat capacity of the film and gas.

---

* Energy and enthalpy are equal at $T = 0°K$

Calculation of ΔH_c:

$$\Delta H_o = \frac{n}{2} NE_o, \tag{14}$$

where n is the coordination number for the array of atoms which make up the film, N is Avogadro's number, and E_o is the minimum internal energy at T = 0 and equal to 13.1×10^{-15} ergs for nitrogen.

In two dimensions a hexagonal close-packed array is formed in which every molecule will be surrounded equidistantly by six others separated by 2r. (r is half the distance between molecular centers.) There are also six next nearest neighbors at a distance of $2\sqrt{3}r$. The second term of Eq. (13) is needed since E_o is defined for the absolute zero of temperature.

As T goes to 0°K, the second term vanishes. For a normal liquid[15] both the rotational and vibrational degrees of freedom are relatively unchanged. Only the translational degrees of freedom are altered. ΔC_p is then given by $\frac{1}{2}$ RT if one considers that one translational degree of freedom is lost. The result is as follows:

Type of interaction	ΔH_o
Nearest neighbors	$24.26 \frac{\text{ergs}}{\text{cm}^2}$
Next nearest neighbors	$1.36 \frac{\text{ergs}}{\text{cm}^2}$
Next next nearest neighbors	$\approx 0 \frac{\text{ergs}}{\text{cm}^2}$
$\int_{0°K}^{77.5°K} \Delta C_p \, dT.$	$3.34 \frac{\text{ergs}}{\text{cm}^2}$

Therefore, $\Delta H_c = 28.96 \frac{\text{ergs}}{\text{cm}^2}$, approximately half the enthalpy of vaporization for the bulk liquid which is expected from bond considerations.

In (b) we evaporate the bulk droplet into the gas phase which requires energy equal to the heat of vaporization ΔH_v. For liquid nitrogen this value is $56.96 \frac{\text{ergs}}{\text{cm}^2}$. In (c) we take the film from an infinite sheet to a drop of bulk liquid. The energy difference in the process is the surface energy of the film which is equal to the difference between ΔH_v and ΔH_c.

The surface energy of a thin film of liquid nitrogen then is $28 \frac{\text{ergs}}{\text{cm}^2}$. This thin film is one molecule deep; therefore, there is a definite and representative area per mole of molecules which makes up the film. A similar calculation for the bulk liquid is complicated by the fact that the depth of the surface zone is unknown in many cases. It is not possible then to speak of a definite area per mole of surface. In addition, this area can be calculated exactly only when the orientation, packing, and molecular geometry in this zone are known. Jura[16] has calculated the surface energy of liquid argon and mercury and found that 78% of this energy is accounted for by the first layer and 99% in the first four molecular diameters. Henniker[17] has discussed the depth of the surface zone in considerable detail.

A similar calculation for a thin film of liquid oxygen[18] leads to a ΔH_c of $41.62 \frac{\text{ergs}}{\text{cm}^2}$[*]. Since ΔH_v for liquid oxygen is $80.61 \frac{\text{ergs}}{\text{cm}^2}$, the surface energy of a thin film of liquid oxygen is $38 \frac{\text{ergs}}{\text{cm}^2}$.

A comparison between the surface energy of a thin film of liquid nitrogen or oxygen with that of the bulk surface energy is possible only

---

[*] Approximately half the enthalpy of vaporization for oxygen.

when the contribution from the first layer to this energy and the depth of the surface is known. For our purposes there is little to be gained by such a comparison. Our calculation of the surface energy of nitrogen or oxygen is not exact, but their magnitude is certainly reasonable. The error on the two values assuming that the lower limit is a face-centered cubic type of packing is $\pm 3 \frac{\text{ergs}}{\text{cm}^2}$. The effect of the crystal structure of substrate on the arrangement of molecules in the thin film has been neglected.

We can now calculate ΔE^{α}_{SL}, the energy of adhesion between a solid and a thin film of liquid (Eq. (6)), and we are ready to develop the equations whereby the relative distribution of energy on the surface can be evaluated.

V. THE DISTRIBUTION OF ENERGY OVER A SOLID SURFACE AT $T > 0^\circ K$

A. Mathematical Description of Technique

The nature of interface between a solid and some other phase, commonly referred to as the surface of the solid, presents a difficult problem. As mentioned, surface imperfections of molecular dimensions (microscopic), such as kinks and surface vacancies, are well established; in fact, at $T > 0^\circ K$ an equilibrium number of them is demanded by the Third Law of Thermodynamics. Furthermore, atoms in irregular positions give rise to microscopic flaws, such as edge and corner atoms. Impurities which are negligible in terms of the overall composition can still make up a major portion of the surface and contribute to this heterogeneity. In addition, the surface is usually made up of various crystal planes having a random orientation. Clearly there will be considerable variation in the surface energy of these planes, and the actual surface energy of the solid is an average of all these energies. Therefore, the fact that the energy over a surface varies from point to point on the surface is not surprising. However, no really satisfactory method has yet appeared in the literature from which by direct experimental observation the relative distribution of the surface energy over this average is given. A method based on the development of Sections III and IV which will give this distribution in terms of the fraction of the surface having energy greater than some specified amount is now presented. The experimental basis will be the net heat of adsorption $[\bar{Q}(\theta)]$ as a function of some preadsorbed material which has a negligible heat of adsorption.[5] This differs from the work of Girifalco,[4] who made use of the heat of wetting defined as

$$\Delta H_W = \bar{\epsilon}_{SL} - \bar{\epsilon}_S(0), \tag{15}$$

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.

This is an integral quantity; the interactions of the wetting liquid are only very slightly involved in the wetting process. Following his approach, let

θ = the fraction of the surface having energy greater than $\epsilon_S(\theta)$.

$\bar{\epsilon}_S(\theta)$= the average energy of that part of the surface having energy equal to or less than $\epsilon_S(\theta)$.

$\epsilon_S(\theta)$ will decrease with increasing θ as shown in Fig. 3a. The average surface energy, $\bar{\epsilon}_S(\theta)$, can be calculated by the following formula:

$$\bar{\epsilon}_S(\theta) = \frac{1}{1-\theta} \int_{\theta}^{1} \epsilon_S(\theta)\, d\theta \tag{16}$$

and is represented by the shaded portion of Fig. 3a. We can now differentiate under the integral sign and solve for $\epsilon_S(\theta)$ in terms of $\bar{\epsilon}_S(\theta)$ and θ. The result is

$$\epsilon_S(\theta) = \bar{\epsilon}_S(\theta) - (1-\theta) \frac{d\,\bar{\epsilon}_S(\theta)}{d\theta}. \tag{17}$$

This equation along with the definition of Φ in Section III will enable us to calculate the relative distribution of energy over the total average energy, $\bar{\epsilon}_S(0)$, as a function of θ. $\bar{\epsilon}_S(0)$ is the average energy of the total surface without any preadsorbate.

We can now use the assumption that a known fraction of the surface θ is covered with a material which is preferentially adsorbed on the high energy sites of the surface. The θ of Eq. (17) and this θ are then identical.

Let $\overline{Q}_{S.A.}$ = the heat of adsorption per cm^2 of N_2 and O_2 on the preadsorbed material (pure stearic acid). This heat should be very small and has been reported to be negligible in a previous paper.[5]

$\overline{Q}(\theta)$ = the net heat of adsorption per cm^2 of surface. The measured heat then is due to the surface masked by the preadsorbate which blocks out the upper range of energies attributed primarily to cracks, dislocations, etc., and to the remaining bare surface. If this filling up of the cracks, pores, etc., lowers the surface area as measured by the B.E.T. method, $\overline{Q}(\theta)$ will then be based on the new surface area available to the adsorbate. In addition, the actual interaction with the pure stearic acid is not critical since the measured heat, $\overline{Q}(\theta)$, includes both the interaction with the preadsorbate and with the covered surface. Figure 3a is now changed to Fig. 3b and Eq. (16) to

$$\overline{\epsilon}_S(\theta) = \frac{1}{\theta}\int_0^\theta k\,d\theta + \frac{1}{1-\theta}\int_0^\theta \epsilon_S(\theta)\,d\theta, \qquad (18)$$

where K is the average surface energy of the covered surface (sample + stearic acid) which will be <u>assumed constant</u>. Equation (17) will not change since the derivative of the first term in Eq. (18) is zero.

From Eq. (9) we have

$$\Phi = \frac{\Delta E^{\alpha}_{SL}}{(\Delta E^{c}_{S}\ \Delta E^{c}_{L})^{1/2}}, \qquad (9)$$

and according to Eq. (7)

$$\Delta E^{\alpha}_{SL} = -\bar{Q}(\theta) + 2\epsilon_L, \tag{7}$$

and

$$\Delta E^{c}_{S} = 2\bar{\epsilon}_S(\theta), \quad \theta(0 \text{ to } 1) \tag{2}$$

$$\Delta E^{c}_{L} = 2\epsilon_L ; \tag{3}$$

therefore,

$$\Phi = \frac{(-\bar{Q}(\theta) + 2\epsilon_L)}{[4\epsilon_L \, \bar{\epsilon}_S(\theta)]^{1/2}} , \; \theta(0 \text{ to } 1) \tag{19}$$

Squaring both sides and solving for $\bar{\epsilon}_S(\theta)$ we have

$$\bar{\epsilon}_S(\theta) = \frac{(-\bar{Q}(\theta) + 2\epsilon_L)^2}{4\epsilon_L \, \Phi^2} . \tag{20}$$

Differentiating Eq. (20) with respect to θ and putting this back into Eq. (17) results in

$$\epsilon_S(\theta) = \frac{(-\bar{Q}(\theta) + 2\epsilon_L)^2}{4\epsilon_L \, \Phi^2} - \frac{(1 - \theta)}{\Phi^2}\left(\frac{\bar{Q}(\theta)}{2\epsilon_L} - 1\right) \frac{d\bar{Q}(\theta)}{d\theta} . \tag{21}$$

Equation (21) was derived to point out that if Φ were known from some independent source, either by some other experiment or theoretical calculation for any given system, it would be possible to calculate the actual distribution over the surface. When the two phases are similar (with respect to their polarity, molecular geometry, density, and type of intermolecular potential functions), it is reasonable to assume that Φ is equal to 1.[4] This is certainly not the general case. Therefore, Eq. (21) cannot be used in this form.

However, resubstituting and arranging terms, results in the following equation:

$$\frac{\epsilon_S(\theta)}{\bar{\epsilon}_S(\theta)} = 1 + \frac{2(1 - \theta)}{(-\bar{Q}(\theta) + 2\epsilon_L)} \quad \frac{d\bar{Q}(\theta)}{d\theta} \quad . \qquad (22)$$

$\frac{d\bar{Q}(\theta)}{d\theta}$ will be known from the slopes of the measured heats as a function of θ.* $\epsilon_S(\theta)/\bar{\epsilon}_S(\theta)$ will be greater than 1 initially, and it will slowly decrease to 1 as the measured heat becomes constant. This will occur at some θ, not necessarily at $\theta = 1$. This is shown in Fig. 4.

Up to this point we have made one assumption; i.e., the average surface energy of the covered surface is constant.

Next, Eq. (19) enables us to calculate a Φ for $\theta = 0$ if we knew the average surface energy of our powder, $\bar{\epsilon}_S(0)$. Since we do not know this value accurately, we would substitute in values which have been obtained either experimentally or theoretically, starting with the lowest possible value to the highest, and would then obtain a large number of Φ's (depending, of course, on our number of $\bar{\epsilon}_S(0)$'s). Doing this it becomes obvious that Φ is rather insensitive to changes in $\bar{\epsilon}_S(0)$. In fact, by changing $\bar{\epsilon}_S(0)$ by 25%, Φ will change by only 7%. We can, therefore, safely say that Φ is relatively constant with θ. For Φ (at $\theta = 0$) constant, we will be able to calculate the change in $\epsilon_S(\theta)$ by the following equation:

$$\frac{(-\bar{Q}(\theta) + 2\epsilon_L)}{(4\bar{\epsilon}_S(\theta)\ \epsilon_L)^{1/2}} = \frac{(-\bar{Q}(0) + 2\epsilon_L)}{(4\bar{\epsilon}_S(0)\ \epsilon_L)^{1/2}} \quad . \qquad (23)$$

---

* Figure 8 of the previous paper.

Rearranging and dividing by $\bar{\epsilon}_S(0)$

$$\frac{\bar{\epsilon}_S(\theta)}{\bar{\epsilon}_S(0)} = \frac{(-\bar{Q}(\theta) + 2\epsilon_L)^2}{(-\bar{Q}(0) + 2\epsilon_L)^2} . \qquad (24)$$

$\bar{\epsilon}_S(\theta)$ will decrease from $\bar{\epsilon}_S(0)$ to some value as measured by $\bar{Q}(\theta)$. [When $\theta = 0$, $\bar{\epsilon}_S(\theta) = \bar{\epsilon}_S(0)$.]

The result will be a curve which will start at 1 and decreases to some value below 1 as shown in Fig. 5 and will be determined <u>solely</u> by the experimental net heats, $\bar{Q}(\theta)$, θ(0 to 1). Now, by multiplying the ordinate of Fig. 5 by the ordinate of Fig. 4, we obtain $\epsilon_S(\theta)/\bar{\epsilon}_S(0)$, which is shown in Fig. 6.

This is the distribution of energy over the surface with respect to some average energy which is not known for the particular sample, but could be measured by some independent experiment. From this analysis we can see what fraction of the surface has high surface energy $\epsilon_S(\theta)/\bar{\epsilon}_S(0) > 1$ and what fraction low surface energy $\epsilon_S(\theta)/\bar{\epsilon}_S(0) < 1$.

If $\bar{\epsilon}_S(0)$ were known, we would be able to calculate the absolute distribution of energy over the surface. The integral of which would be $\bar{\epsilon}_S(0)$ as measured. This can still be done by choosing the "best" possible experimental or theoretical value for $\bar{\epsilon}_S(0)$ and multiplying this value by the ratio $\epsilon_S(\theta)/\bar{\epsilon}_S(0)$ as a function of θ. We feel that this is not necessary and should be done only when reliable surface energies can be obtained experimentally and in agreement with theoretical calculations.

B. Summary

This method is both unique and simple. The two assumptions made are reasonable; namely, the surface energy of the sample + stearic acid, K, and Φ are constant. The latter will be shown to be true from experimental heat data, $\overline{Q}(\theta)$, as a function of the fraction of the surface covered with acid (θ).*

The preadsorbate does not completely destroy the effect of the underlying surface; that is, there is still a force of attraction between the covered surface and the gas. The initial force ($\theta = 0$) is reduced to some fraction of its original value. In addition, the form of the equation for Φ, Eq. (19), is such that the error on Φ will always be small (approximately 10%).**

The experimental heat, $\overline{Q}(\theta)$ is a "net heat" and is a measure of the interaction between the gas and the solid only. The contribution from lateral interactions has been subtracted out by the third term (ΔH_s) in Eq. (5) which is approximately the heat of condensation at the monolayer (56.96 ergs/cm^2 for bulk liquid nitrogen).

---

* This was found to be true for work done on $BaSO_4$ which will be published in a separate paper.

**By putting in different values for $\overline{\epsilon}_S(0)$ [Eq. (19)], Φ did not change by more than 10%.

VI. RELATIVE DISTRIBUTION FOR TiO_2 SAMPLE

The results for the TiO_2 sample are shown in Table I and Figs. 7 and 8. Only approximately 15% of its surface has energy greater than the average. After $\theta_{11} = .50$, the surface is homogeneous.

Figure 8 is in good agreement with the theoretical work of Aston[19] who adopted a model of many-sided sites on the surface of TiO_2 in order to explain the nature of its heterogeneity. By straightforward statistical mechanical considerations he derived expressions for the adsorption isotherm and the differential heat of adsorption. Only four types of sites were used: four sided, three sided, two sided, and one sided with energies ϵ_4, ϵ_3, ϵ_2, and ϵ_1; and $\epsilon_4 = 4\epsilon_1$, etc. Lateral interactions were taken into account on the two- and one-sided sites only. He obtained good qualitative agreement with this theory and the experimental data on the TiO_2-Ne system. Any discrepancy was attributed to the fact that the two-sided sites take part in lateral interactions which are more complicated than postulated, and that sites of intermediate energy are present on the surface. In Fig. 8 the distribution starts at approximately 4 as it should according to the model of Aston.[19] He also found that the four-sided sites make up a negligible fraction of the surface. If $\bar{\epsilon}_S(0)$ were known, we could calculate the energy of these sites on the surface. The shape of the distribution obtained in this work is also very similar to that found by Honig and Reyerson.[20]

Table I.

The relative surface energy distribution of TiO_2 calculated from net heat of adsorption measurements as a function of preadsorbed stearic acid at T = 83.9°K, sample T.

θ_{11}	$\overline{Q}\left(\frac{\text{ergs}}{\text{cm}^2}\right)$	$\frac{d\overline{Q}}{d\theta}\left(\frac{\text{ergs}}{\text{cm}^2}\right)$	$\frac{\epsilon_S(\theta)}{\overline{\epsilon}_S(\theta)}$	$\frac{\epsilon_S(\theta)}{\overline{\epsilon}_S(0)}$
0	53.80	119.5	3.92	3.92
.189	36.53	107.60	1.83	1.170
.513	26.91	0	1	.47
.713	26.91	0	1	.47

VII. CONCLUSIONS AND DISCUSSION OF ERROR

The distribution presented for TiO_2 represents the general shape of the energy distribution. This distribution is relative to the average surface energy of the powder and does not evaluate the absolute energy spectrum on the surface. If $\bar{\epsilon}_S(0)$ were known and a value of K either assumed or calculated from an additional experiment (such as, heat of solution), then the absolute spectrum of energies on the surface could be obtained. This distribution would be one based solely on well-defined thermodynamic data, and these basic results would not be subject to a large error.

The fact that ratios (Eqs. (22) and (24)) were used will tend to reduce error. The error on the slope $d\bar{Q}/d\theta$ was found to be approximately 8%. The error on $2\epsilon_L$ is 10%. The error on $\bar{Q}(\theta)$ is, of course, variable; that is, at $\theta = 0$ it is approximately 2% and after θ approximately = .60 is as high as 10%. $\bar{Q}(\theta)$ is then constant with θ, and $d\bar{Q}(\theta)/d\theta$ is zero; therefore, the error in $d\bar{Q}(\theta)/d\theta$ is only important in the heterogeneous portion of the surface. The error on $\epsilon_S(\theta)/\bar{\epsilon}_S(0)$ calculates to be about 14% initially ($\theta = 0$) and as high as 20% in the homogeneous portion. It is very difficult to compare these errors with the uncertainty of the distributions presented in the past since their results are based on a model and a mathematical description in terms of arbitrary parameters of the adsorption isotherm.[1,2] The newest approach used to obtain a site energy distribution from the experimental isotherm is graphical,[3] and successive approximations to the fraction of the surface whose site energy is equal to or greater than some specified value are made. This method is very tedious and should be programmed for practical use. Since a graphical derivative is one of the operations of the method, the uncertainty on the final distribution is subject to an error of the same magnitude as the present technique. In addition, it arbitrarily assumes a local isotherm such as the Langmuir,[21] and the resulting distribution is very insensitive to a change in the original assumed isotherm such as one in which lateral interactions are taken into account.[22] The assumptions used in order to derive Eqs. (22) and (24) have been carefully explained. One of these assumptions was actually verified experimentally;[*] that is, the assumption of a constant surface energy for the combination (sample + stearic acid). The second assumption (Φ constant) was shown to be reasonable because of the form of the equation for Φ and the fact that a large error does not result if Φ is not constant with coverage. In addition, Eqs. (22) and (24) can be easily used on any system where $2\epsilon_L$ is known or calculable, and heats of adsorption as a function of some preadsorbed substance (gas or solid) can be measured. This is possible with a common adsorption apparatus.

Therefore, the results presented here are meaningful and are the first direct measurement on the relative distribution of surface energy on a fine powder surface by means of physical adsorption studies without the use of any model, arbitrarily assumed isotherm, etc. Lateral interactions were also taken into account by the present method. In addition, the results obtained agree with what is presently known concerning the nature of the surface for TiO_2.

---

[*] Paper to be published.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge L. A. Girifalco for his insight and experience in the theoretical aspect of this work. We also wish to thank the National Institute of Health for its generous support. The work was also supported in part by the United States Atomic Energy Commission.

REFERENCES

1. R. Sips, J. Chem. Phys. 16, 490 (1948).
2. J. M. Honig, J. Chem. Phys. 24, 510 (1956).
3. A. W. Adamson and I. Ling, Solid Surfaces and the Gas-Solid Interface, in Advances in Chemistry, Vol. 33 (American Chemical Society, Washington, D.C., 1961) p.51.
4. L. A. Girifalco, M. S. Thesis, University of Cincinnati (1952).
5. J. M. Morabito, P. F. Duby and L. A. Girifalco, this journal.
6. R. Fowler and E. A. Guggenheim, Statistical Thermodynamics (Cambridge University Press, Cambridge, England, 1949), Chapter X.
7. W. D. Harkins and G. Jura, in Colloid Chemistry, J. Alexander, editor, (Reinhold Publ. Co., New York, 1946), Vol. VI, p. 1-76.
8. W. D. Harkins, J. Chem. Phys. 10, 268 (1942).
9. R. Shuttleworth, Proc. Phys. Soc. (London) A63, 447 (1950).
10. C. Herring, Phys. Rev. 82, 87 (1951).
11. L. A. Girifalco and R. J. Good, J. Phys. Chem. 61, 904 (1957).
12. R. J. Good and L. A. Girifalco, J. Phys. Chem. Solids 10, 99 (1959).
13. J. H. Hildebrand and R. L. Scott, Solubility of Non-electrolytes, 3rd edition (Dover Publications, New York, 1964) p. 230.
14. E. A. Moelwyn-Hughes, Physical Chemistry, 2nd edition (Macmillan Co., New York, 1964), Chapter VII.
15. J. H. Hildebrand and R. L. Scott, Solubility of Non-electroyltes, 3rd edition (Dover Publications, New York, 1964) p. 67.
16. G. J. Jura, J. Phys. Chem. 52, 40 (1945).
17. J. C. Henniker, Rev. Mod. Phys. 21, 322 (1949).

18. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc., New York, 1954).

19. 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).

20. J. M. Honig and L. H. Reyerson, J. Phys. Chem. 56, 140-4 (1952).

21. I. Langmuir, J. Amer. Chem. Soc. 40, 1361 (1918).

22. P. Y. Hsieh, J. Phys. Chem. 68, (5) 1068 (1964).

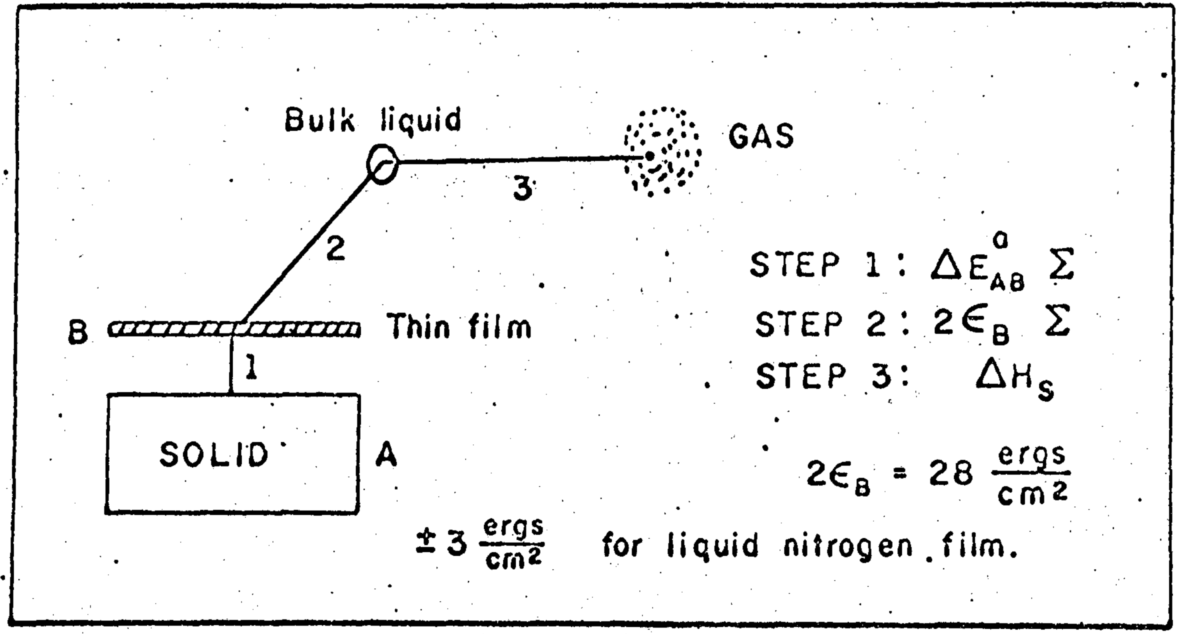


FIG. 1 The thermodynamic cycle of equation 4.4.

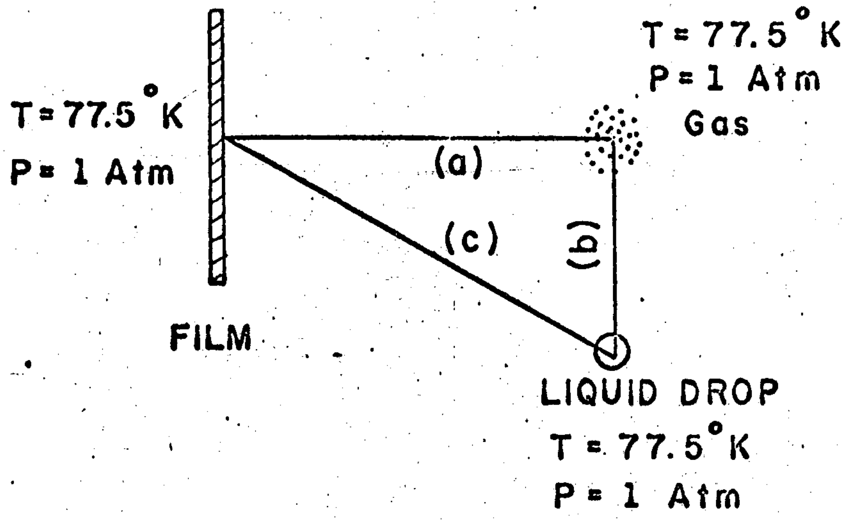


FIG. 2 The thermodynamic cycle used to calculate the surface energy of a thin film.

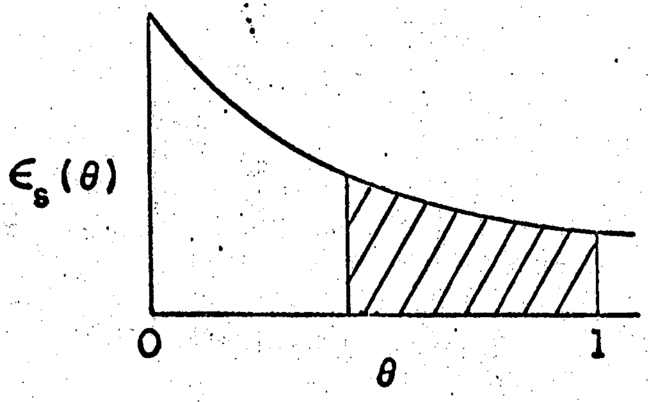


FIG. 3a $\epsilon_s(\theta)$ versus θ.

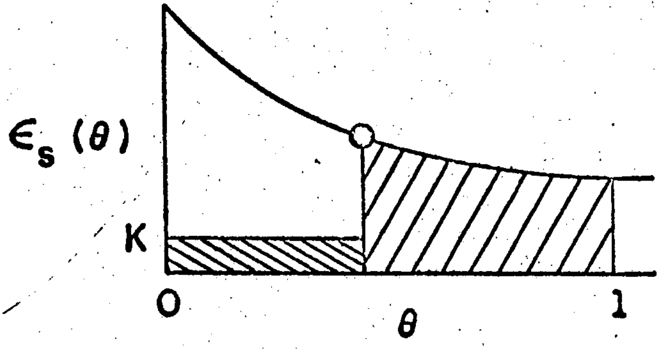


FIG. 3b $\epsilon_s(\theta)$ versus θ.

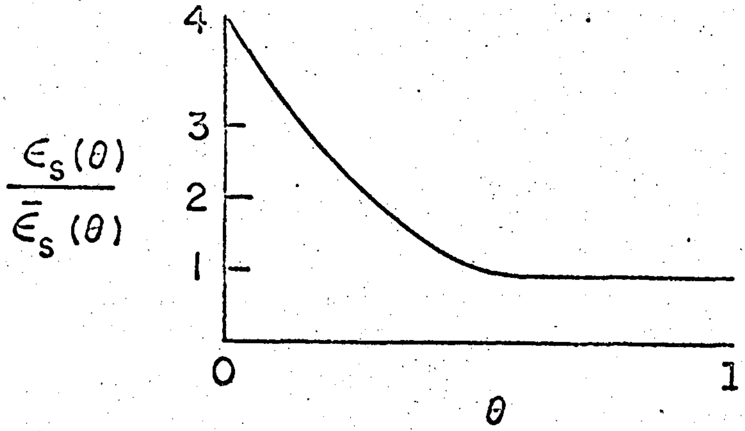


FIG. 4 $\frac{\epsilon_s(\theta)}{\bar{\epsilon}_s(\theta)}$ versus θ.

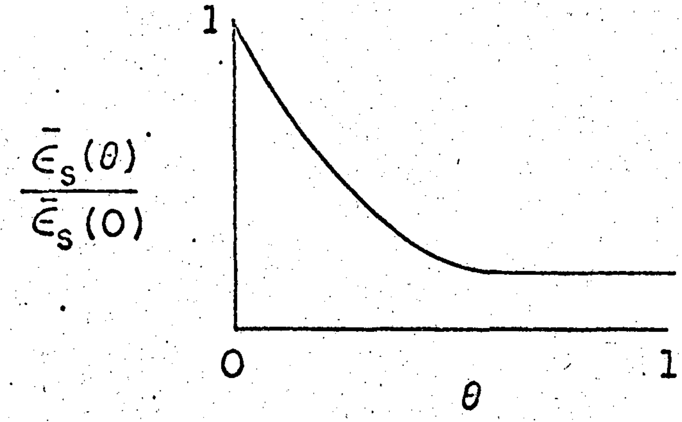


FIG. 5 $\frac{\bar{\epsilon}_s(\theta)}{\bar{\epsilon}_s(0)}$ versus θ.

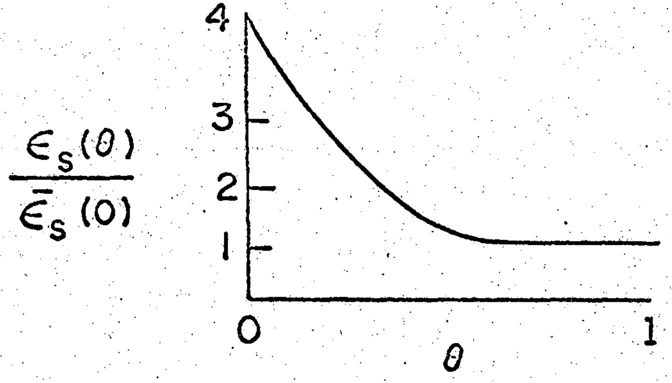


FIG. .6 $\frac{\epsilon_s(\theta)}{\bar{\epsilon}_s(0)}$ versus θ.

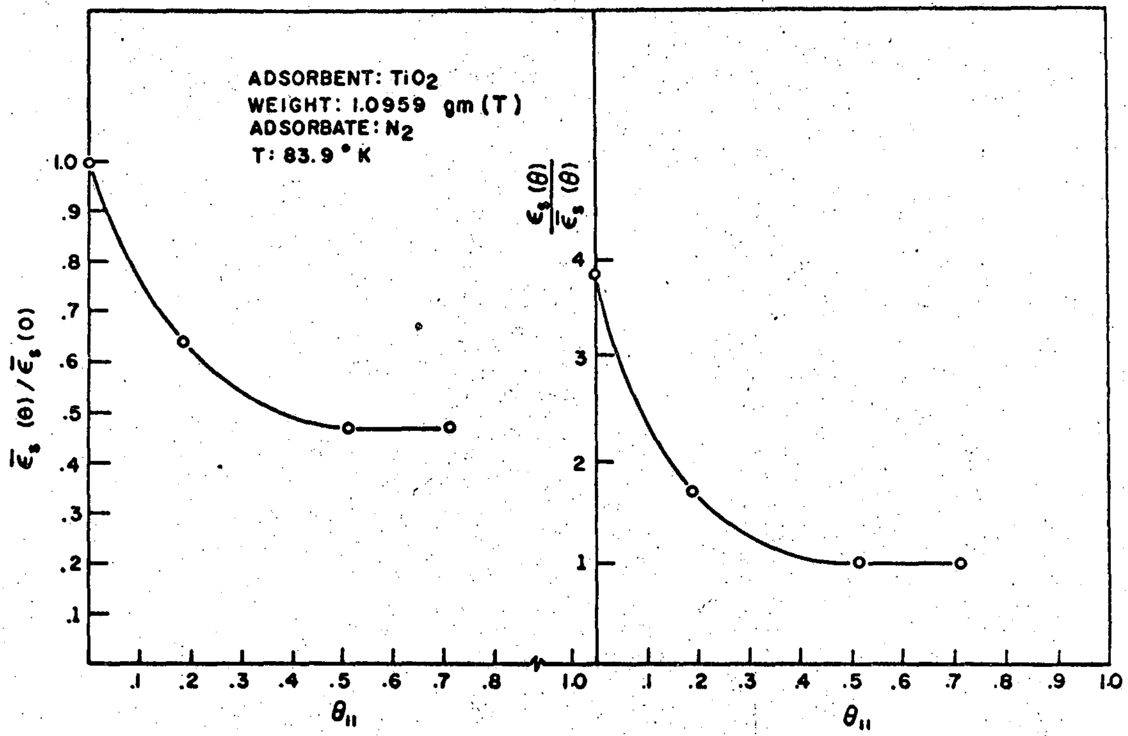

ADSORBENT: TiO2
WEIGHT: 1.0959 gm (T)
ADSORBATE: N2
T: 83.9 ° K
$\bar{\epsilon}_s(\theta)/\bar{\epsilon}_s(0)$
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.1 .2 .3 .4 .5 .6 .7 .8 1.0
θ_{11}
$\frac{\epsilon_s(\theta)}{\bar{\epsilon}_s(\theta)}$
4
3
2
1
.1 .2 .3 .4 .5 .6 .7 .8 .9 1.0
θ_{11}

Fig. 7

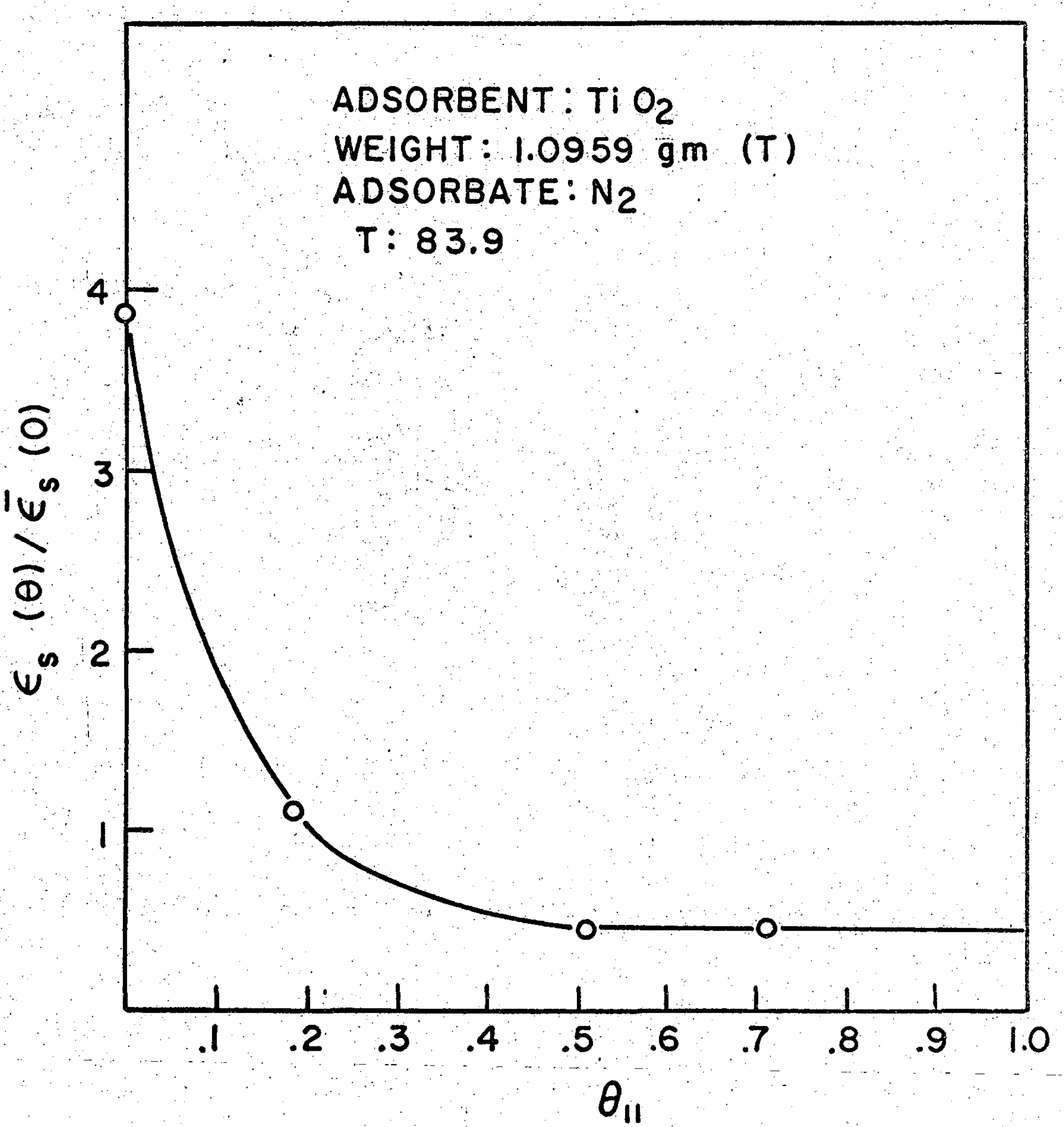

ADSORBENT : Ti O_2
WEIGHT : 1.0959 gm (T)
ADSORBATE : N_2
T : 83.9
$\epsilon_s\ (\theta)/\bar{\epsilon}_s\ (0)$
4
3
2
1
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
θ_{11}

Fig. 8