

Graphical integration is recommended as simple and accurate, and it is shown that it is essential to obtain many experimental points in the low pressure region.

2. A method is described whereby the pressure can be determined to 0.002 mm. with a mercury manometer.

3. Data are given for the lowering of the free surface energy of TiO_2 (anatase) by nitrogen at -195.6° , water at 25.0° , *n*-heptane at 25.0° , and *n*-butane at 0.0° as a function of the relative pressure of the adsorbed vapors.

4. The spreading coefficient, free energy of emersion, and work of adhesion of nitrogen, water, *n*-butane and *n*-heptane on TiO_2 (anatase) have

been determined. The spreading coefficients are found to be 56, 190, 43 and 46 erg cm^{-2} for nitrogen, water, *n*-butane, and *n*-heptane on TiO_2 (anatase). The spreading pressures of nitrogen and of normal butane on a porous solid are given. These films show the same phases and phase transitions shown by insoluble films on liquid subphases.

5. It is shown that for nitrogen at -195.8° , the lower the vapor pressure of the monolayer, the higher its film pressure. It is found that the film pressure of the monolayer varies from 20.6 to 29.8 ergs cm^{-2} when the relative vapor pressure is varied from 0.114 to 0.081.

CHICAGO, ILLINOIS

RECEIVED APRIL 15, 1944

[PAPER NO. 111 OF THE LABORATORY OF SURFACE CHEMISTRY, CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND THE UNIVERSAL OIL PRODUCTS COMPANY]

Surfaces of Solids. XII. An Absolute Method for the Determination of the Area of a Finely Divided Crystalline Solid

BY WILLIAM D. HARKINS AND GEORGE JURA

I. Introduction: Purpose of the Absolute Method for the Determination of the Area of a Solid

Undoubtedly, the greatest single factor that for many years impeded the study of the properties of the surface of solids was the inability to determine the absolute, or even the relative, areas of finely divided solids. In this paper there is described a calorimetric method which gives the absolute area of a finely divided crystalline solid. This method was developed, not to give a simple procedure for common use, but to provide a standard for the measurement of surface areas. With crystalline solids of a suitable fineness, the values obtained are much more accurate than those obtained by any other known method. By the application of differential calorimetry, much more accurate values can be obtained than with the ordinary calorimetry used thus far in our work. The method and the results should convince those who doubt that there is any reality in the value of the area of a finely divided solid, that their point of view is not justified, at least not for such solids as those to which this method can be applied.

It is true that the measured area of a rough piece of ground depends upon the conventions adopted for its measurement and, according to the nature of these conventions, may depend upon the nature of the instruments employed for the measurement. When the purpose for which the area of a solid is determined, is associated with the actions of molecules upon its surface, it seems that molecules should be the instruments best adapted for the measurement of area.

In both the absolute calorimetric method de-

scribed here and in the relative vapor absorption method of paper XIII, which follows, molecules are used for the determination of the area of a solid, but in neither is a knowledge of the area occupied by the molecules required nor involved. The absolute method is applicable to non-porous solids only, while the relative method is accurate for porous solids also.

The calorimetric method depends upon a relation never before utilized for this purpose. Its principal practical use at present is to determine the value of the constant needed to give the area of a solid when our relative method is used. For very fine crystalline solids the absolute method gives, even now, much more accurate values of the area than any other procedure, and with the use of differential calorimetry the same accuracy can be extended to much coarser powders, as indicated later.

II. General Method

Both the general theory of solids and electron microscope photographs agree in indicating that very fine crystals do not exhibit cracks, such as may be found in larger crystals. If such a small crystal is suspended in the saturated vapor of a liquid, it becomes coated with an adsorbed film (Fig. 1). If this liquid gives a zero angle of contact with the solid, the adsorbed film thickens, until at equilibrium its surface energy becomes the same as that of the liquid in bulk. It is predicted that the crystal is not so small as to cause an appreciable change of surface energy due to curvature.

The system is allowed to come into thermal equilibrium in a sensitive calorimeter. Then the

crystal, coated with its adsorbed film, is dropped into the liquid. Suppose, for example, that the liquid is water with a surface energy (h_L) of 118.5 erg cm.⁻²; then the only energy change involved is that due to the disappearance of the water surface of the adsorbed film. If the energy developed in the calorimeter, expressed in ergs, is now divided by 118.5, the quotient gives the area of the surface of the particle with its adsorbed film of water. To obtain a knowledge of the area of the uncoated particle it is necessary to make a very small correction for the thickness of the adsorbed film.

In the actual experiments enough particles are used to make it possible to obtain the mass of the adsorbed film by weighing on a balance. From the mass of the film, the density of the liquid, and the area of the outer part of the film, the mean equivalent thickness of the film can be calculated. This is the thickness which the film would have, provided its density is that of the liquid itself, which is nearly true for the outer part of a duplex film, although the density of the first molecular layer next to the solid (and even of the second layer) may be somewhat different. However, if a liquid such as water, which gives a somewhat thin duplex film, is employed, this correction may be made small, and since its magnitude is known moderately well, the total error is largely that of the calorimetric work.

It is obvious, however, that if either too small crystals, or too thick a duplex film is used, this error may be so large as to give unsatisfactory results. Our thermals are sensitive to about $2 \times 10^{-5}^\circ$, and the calorimetric system, designed to determine the energy of immersion of solids with clean surfaces, is not sufficiently sensitive to give a high degree of accuracy in this type of work unless the area of the crystalline solid is higher than 10 m.²g.⁻¹ when the density is about 4. With the proper differential calorimeter, which should be used in this work, the applicability of the method could be greatly extended; such crystalline powders of this density would give accurate values at areas as small as 1 m.²g.⁻¹. The value of the area of the uncoated sample of anatase was found by this absolute method in which immersion in water was employed, to be 13.8 square meters per gram, while the method of Brunauer, Emmett and Teller which uses an adsorption isotherm, gave 13.9 square meters per gram by the use of Emmett's usual assumption of 16.2 sq. Å. as the area per nitrogen molecule in the complete monolayer.

Thermodynamic Theory

The heat of emersion per sq. cm., $h_{E(SL)}$, of a clean solid in a liquid is given by the relation

$$h_{E(SL)} = \gamma_S - \gamma_{SL} - T(\partial\gamma_S/\partial T - \partial\gamma_{SL}/\partial T)_p, \Sigma_{S,SL} \quad (1)$$

where γ_S is the free surface energy of the solid, γ_{SL} the free interfacial energy of the solid-liquid interface, and T is the absolute temperature. If

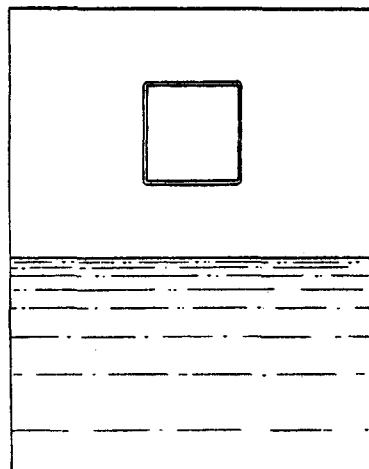


Fig. 1.—Crystal in equilibrium with the vapor of a liquid: to be immersed in the liquid and thus lose the surface energy of the duplex film of liquid.

the solid is exposed to the saturated vapor of the liquid until the adsorbed film attains equilibrium with respect to the vapor, the free surface energy changes from γ_S to γ_{S_0} while the surface enthalpy is changed from $h_{E(SL)}$ to $h_{E(S_0L)}$. The heat of emersion of the solid saturated with the vapor then becomes

$$h_{E(S_0L)} = \gamma_{S_0} - \gamma_{S_0L} - T(\partial\gamma_{S_0}/\partial T - \partial\gamma_{S_0L}/\partial T)_p, \Sigma \quad (2)$$

Eq. 2 may be simplified by the use of the relationship¹

$$\gamma_{S_0} = \gamma_L + \gamma_1 \cos \theta \quad (3)$$

If Eq. 3 is substituted in Eq. 2, it is found upon simplification that

$$h_{E(S_0L)} = \left(\gamma_L - T \frac{\partial\gamma_L}{\partial T} \right) \cos \theta + T\gamma_1 \sin \theta \frac{\partial\theta}{\partial T} \quad (4)$$

where θ is the contact angle of the liquid on the solid. If it is assumed that $\theta \approx 0$, it is found that

$$h_{E(S_0L)} = \gamma_L - T\partial\gamma_L/\partial T = h_L \quad (5)$$

The right-hand side of Eq. 5 is simply the heat content of the surface of the liquid used. This quantity can be obtained from the surface tension and temperature variation of the surface tension of the liquid.

The outer area of the film (Σ'), in equilibrium with the saturated vapor of the liquid is not much larger than that (Σ) of the clean solid. The value of Σ' is given by the relation

$$\Sigma' = 4.185 \times 10^7 H_{E(S_0L)}/h_L \quad (6)$$

where $H_{E(S_0L)}$ is the heat of emersion of the film-covered powder in cal. g.⁻¹. This is the same relation obtained in the general discussion of the previous section.

If it were possible to work with a single plane surface, Σ' would be equal to Σ , the specific area of the clean solid surface. If the material is por-

(1) W. D. Harkins and H. K. Livingston, *J. Chem. Phys.*, **10**, 342 (1942)

ous, it is apparent that Σ' will be much less than Σ . This is due to the filling up of the pores, thus greatly reducing the surface area exposed. The measured value for the heat of emersion may then be so small as to appear to be zero, as reported by Razouk,² who found that charcoal saturated with methyl alcohol gave a zero heat of emersion.

If, however, the solid is non-porous and crystalline, the area of the clean solid surface, Σ , can be obtained from the area of the film-covered surface. The method of obtaining the area of the clean solid from that of the film-covered solid will be discussed in a later section.

III. Experimental

Materials.—Two samples of TiO_2 (anatase) were used in this work. The first of these was an oil-free sample, which has been described in paper X. The second sample was treated with aluminum trioxide by a method not disclosed to the authors. However, the fact that the surface properties have been radically altered is shown in the next section. The changes, if any, brought about in the crystal structure were too small to be detected by X-ray diffraction, since both the treated and the untreated samples gave identical patterns. The water used in the work was double distilled, the second distillation being carried out over acid permanganate.

Apparatus.—The apparatus employed for the determination of the isotherm and the heat of emersion has been described in previous papers³; that used for the preparation of the samples for the calorimetric work is shown in Fig. 2.

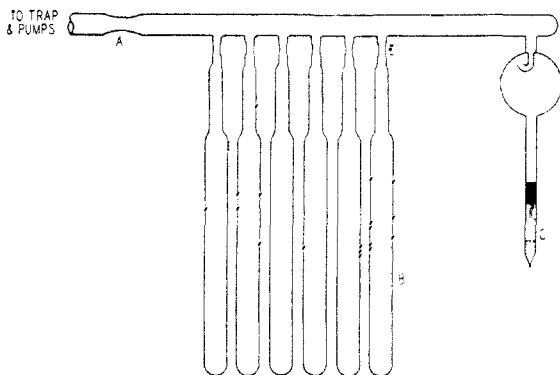


Fig. 2.—Apparatus for the adsorption of an equilibrium film on a powder. C indicates the liquid. The six tubes are filled with the powder.

Between 10 and 15 g. of the powder is placed in each of the sample bulbs B, of which there are usually six, and 5 to 10 cm.³ of water is placed in C. The water is degassed by boiling away about one-half of the original volume and then sealing the bottom of the bulb. The tubes which contain the powder are heated in an electrically heated furnace at 500° for twenty-four hours, after which they are allowed to cool to room temperature. The pumps are in continuous operation during this period. After the samples have cooled, the whole manifold is sealed off at C, and the whole apparatus is submerged in a thermostat at 25.00°. After four hours in the thermostat, the tip of C is broken with an iron rod and a magnet. This allows the water vapor to penetrate the entire system. After about twenty-four hours, which is more than sufficient time for the

system to reach equilibrium, the manifold is raised and the sample tubes are sealed off at E.

IV. Results and Discussions

The results of the calorimetric measurements⁴ of the heats of emersion of the two samples are summarized in Table I, while the adsorption isotherms of water are shown in Fig. 3. The average

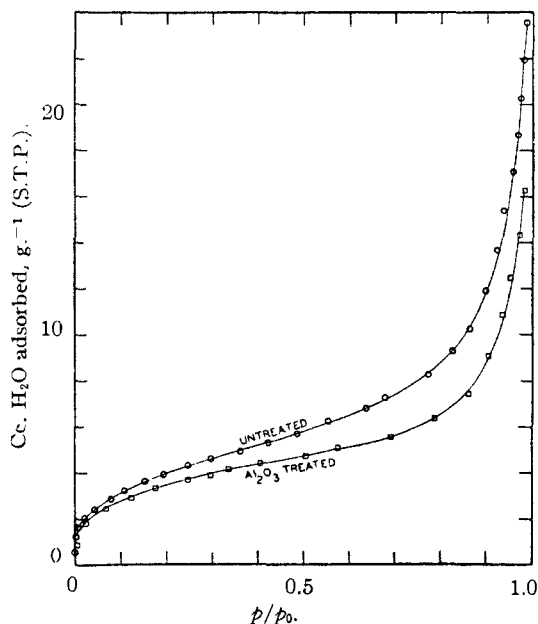


Fig. 3.—Adsorption isotherms of water on crystalline solids, $t = 25.0^\circ\text{C}$.

deviation of the values of the heats of immersion of the clean powders was 1%, while that of the saturated powders was 3%. The area of the treated sample is so low that the determination of the heat with our present equipment is not very accurate. If the powder is clean, the apparatus is capable of going to lower heat values than the 0.25 cal. g.⁻¹, which was the heat value found for the saturated powder. However, the greater difficulty of dispersing the saturated powder necessitates the use of smaller samples than can be used with the clean powder.

TABLE I

TiO_2	AREA (Σ) OF POWDERS BY THE ABSOLUTE METHOD				
	$H_E(\text{SL})$	$h_E(\text{SL})$	$H_E(\text{S}_c\text{L})$	Σ'	Σ
Untreated	1.69	510	0.409	14.4	13.8
Coated with Al_2O_3^a	1.43	630	0.257	9.07	8.9

^a The error in the determination of the area of this sample is greater than for the other, since the area is somewhat low for our present calorimeter.

This value for the powder of lower area is not so accurate as that for the high-area powder. The

(4) The calorimeter was of the type used by Harkins and Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930), and the technique employed was similar to that used by Boyd and Harkins, *THIS JOURNAL*, **64**, 1190 (1942). A 36 junction copper-constantan thermel, with a sensitivity of 0.00002°, was employed.

(2) R. I. Razouk, *J. Phys. Chem.*, **45**, 190 (1941).

(3) W. D. Harkins and G. Jura, *THIS JOURNAL*, **66**, 919 (1942); **66**, 1356 (1944).

error is such as to make the area too low. In the calculation of $h_{E(SL)}$, the area obtained from the nitrogen adsorption isotherm, $9.6 \text{ m.}^2\text{g.}^{-1}$, was used. The values of $h_{E(SL)}$ show that the treatment with aluminum oxide had a marked effect on the properties of the surface, since it increased the heat of emersion from 510 to 630 erg cm.^{-2} . The area of the solid covered by the film was obtained by using a value of $118.5 \text{ erg cm.}^{-2}$ for h_L , the enthalpy of the water surface.⁵ Unfortunately the calculation of the difference between the area of the clean and the film-covered powder is not very exact, but fortunately this affects only the correction term. By making divers reasonable assumptions the area of the clean powder may vary on this basis from $13.5 \text{ m.}^2\text{g.}^{-1}$ to $14.1 \text{ m.}^2\text{g.}^{-1}$; therefore, the area of the clean powder is taken as $13.8 \text{ m.}^2\text{g.}^{-1}$. The average deviation of the results from the average is $0.4 \text{ m.}^2\text{g.}^{-1}$. Thus the value chosen is within experimental error of the limits of probable variation of the correct result.

In calculating the correction it was assumed that the individual powder particles are cubes. After the adsorption has taken place, the diameter of the cube would be increased to $d + 2\tau$, where d is the diameter of the cube and τ is the average thickness of the film. It is then apparent that the two areas are related by the equation

$$\Sigma = \Sigma' / \left(1 + a \frac{\tau}{d}\right)$$

where a depends on the manner in which the average diameter is obtained and the shape of the adsorbed film on the cube. The value of τ was assumed to be 20 \AA . This value was obtained from Σ' and the amount of water adsorbed at saturation. It is apparent, however, that a 25 or 50% variation in τ will not affect the result by more than 2-4% for this sample. The maximum value obtained for a was 4. This value was obtained by assuming that the particle covered with the film is also a perfect cube whose edge is $d + 2\tau$. Now d as obtained from the uncorrected area and density of the sample was found to be 1200 \AA . If it is assumed that the film forms a cylinder around the edge of the cube, a assumes the value of π .

An alternative method of calculating a is by assuming that the particle size of the sample can be represented by a distribution function of the form

$$N = Ce^{-bd^2}$$

The area of the sample is then calculated from the distribution. If it is assumed that the particles with the adsorbed film are cylindrical around the edge, the minimum value of a is obtained as $\pi/2$. The same value of d is again used. Other methods of evaluating a were used. However, all the

(5) Calculated from the surface tension data of P. L. K. Gross, Ph.D. Thesis, "The Theory of Atomic Collision, The Determination of a Standard for Surface Tension Measurements," University of Chicago, 1926.

values ranged between the maximum and minimum values given. This treatment has not been exhaustive, but the correction is certainly within the present experimental error of determination of the other values.

Since it is apparent that the correction to be applied is proportional to τ/d , it is evident that the necessary correction can be made smaller by using coarser powders and differential calorimetry. Unfortunately at this time it is not possible to take the time from more essential work to make this change. By using a differential calorimeter, as mentioned earlier, it would be possible to work with total areas that are about 0.02 of that now required. This would mean that the average value of d could be increased by a factor of 3 to 4. Since for a given material τ would not be expected to vary, the necessary correction would become negligible. The comparison of the areas obtained calorimetrically with those obtained from the adsorption of nitrogen by the theory of Brunauer, Emmett and Teller, shows that there is excellent agreement. Their nitrogen areas are based upon the assumption that the area of the nitrogen molecule is 16.2 sq. \AA . The areas of the powders determined calorimetrically are 13.8 and $8.9 \text{ m.}^2\text{g.}^{-1}$, while the nitrogen adsorption gave 13.9 and $9.6 \text{ m.}^2\text{g.}^{-1}$. From this it is concluded that when nitrogen is the adsorbate the theory of Brunauer, Emmett and Teller gives reliable results for the areas of solids.

Summary

1. An absolute method has been developed for the determination of the area of a solid covered with a film in equilibrium with the vapor of liquid at the saturation pressure of the liquid. The area Σ' is given by the relationship

$$\Sigma' = 4.185 \times 10^7 H_{E(S,L)} / h_L$$

where $H_{E(S,L)}$ is the heat of emersion of the saturated powder in cal. g.^{-1} and h_L is the "total energy" of the surface of the liquid. The equation is valid only if the contact angle is zero. Thus the liquid employed must be chosen so that this condition is met.

2. If the solid is non-porous, *i. e.*, a finely divided crystal, the area of the clean powder can be obtained from the area of the saturated powder by the relationship

$$\Sigma = \Sigma' / \left(1 + a \frac{\tau}{d}\right)$$

where Σ (very nearly equal to Σ') is the area of the clean powder, τ the thickness of the film, and d is the edge of the average crystal cube.

3. The areas of two different samples of TiO_2 were determined by this method. The areas found for these samples were 13.8 and $8.9 \text{ m.}^2\text{g.}^{-1}$, while the theory of Brunauer, Emmett and Teller applied to the adsorption of nitrogen on these samples gives 13.9 and $9.6 \text{ m.}^2\text{g.}^{-1}$, respectively,

provided that Emmett's usual assumption of 16.2 sq. Å. as the area of the nitrogen molecule is adopted. On account of the much higher accuracy in the calorimetry with the sample of area

13.8 m.²g.⁻¹, this is the only result which should be compared with that obtained by us by the method of B. E. T.

CHICAGO, ILLINOIS

RECEIVED APRIL 28, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND THE UNIVERSAL OIL PRODUCTS COMPANY, PAPER 112 OF THE LABORATORY OF SURFACE CHEMISTRY]

Surfaces of Solids. XIII. A Vapor Adsorption Method for the Determination of the Area of a Solid without the Assumption of a Molecular Area, and the Areas Occupied by Nitrogen and Other Molecules on the Surface of a Solid

BY WILLIAM D. HARKINS AND GEORGE JURA

I. Introduction

In 1938 Brunauer, Emmett and Teller¹ (BET) developed a kinetic theory of adsorption, which makes it possible to calculate from an adsorption isotherm, in which the pressure is given as a function of the amount of vapor adsorbed, the number (N) of molecules of vapor necessary to complete a monolayer on the surface of a solid. It is obvious that this would make it possible to calculate the area of the surface provided the mean area occupied per molecule in the completed monolayer were known.

In the section which follows, a method is developed by means of which the area of a solid may be obtained without the use of a molecular area. It is obvious that if the number (N) of molecules required to cover the surface of a gram of solid, and (Σ), the area of the solid are both known, then the mean area (σ) per molecule is given by the relation

$$\sigma = \Sigma/N \quad (1)$$

and

$$\Sigma = N\sigma \quad (2)$$

In the BET procedure it is necessary to use Eq. 2, and since Eq. 1 involves Σ , the area which is to be determined, it is necessary for them to estimate the molecular area in some other way. This was done² by the use of the equation

$$\sigma = (4) (0.866) (M/4 \sqrt{2} A \rho)^{2/3}$$

which assumes close packing in the surface. Here ρ represents the density of the solid or of the liquid adsorbate, M is the molecular weight, and A is Avogadro's number. This equation gave the following molecular areas: 16.24 sq. Å. for nitrogen (liquid) at -195.8° , 13.8 sq. Å. (solid) at -252.5° , and 32.1 sq. Å. for butane (liquid) at 0° . These values are important in connection with a later discussion of molecular areas. It is remarkable that when either of the two molecular areas of the nitrogen molecule is used, the values of the areas of solids obtained by their method

and by ours, are as closely in agreement as is possible when the areas involved are as divergent as 13.8 and 16.2 sq. Å. per molecule. However, the error in the area (Σ) of a solid produced by the uncertainty in the molecular areas used in their method is small when compared with the error in methods earlier than theirs.

It is customary for Emmett to use the area 16.2 sq. Å., as obtained from the liquid, and in paper XII of this series it is shown that a sample of crystalline anatase (TiO_2) gave an area of 13.9 sq. meters per gram by their method on the basis of this molecular area for nitrogen, while our extremely different absolute method gave 13.8 sq. meters per gram. As tested by the methods developed by us, the BET method is remarkably well adapted to the determination of the area of solids. However, when porous solids of the type of silica alumina gels are under investigation, somewhat lower values for the area of the nitrogen molecule, as given later, give better agreement with the areas of such solids, when these are determined by the new method.

II. Experimental Methods for the Determination of the Adsorption Isotherm

For the determination of the areas of solids in general the most suitable vapor is that of nitrogen, provided either nitrogen or air is available in the liquefied form. Argon may be used if preferred. The apparatus and technique used for the determination of the isotherms of liquids such as water and *n*-heptane at 25° , which have low values of p_0 , the vapor pressure at saturation, are described in an earlier contribution.³

A diagram of the apparatus for the determination of the nitrogen isotherms is exhibited in Fig. 1. The part of the apparatus used for the higher pressures is the same in its essential features as that of Emmett and Brunauer.⁴ The variations in technique and design are not of a major type, but they contribute markedly to the precision of the results and are, therefore, important. The diagram shows also the attachment and necessary stopcocks for the use of either the low or higher pressure manometer. The changes in design are the addition of (1) a vapor pressure thermometer as described in the following paragraph, of (2) a wide bore, 25-mm. diameter, manometer for low pressure work, and the use of (3) only one U-tube before the sample, thus decreasing the dead space.

(1) S. Brunauer, P. H. Emmett and E. Teller, *THIS JOURNAL*, **60**, 309 (1938).

(2) P. H. Emmett and S. Brunauer, *ibid.*, **59**, 1553 (1937).

(3) G. Jura and W. D. Harkins, *ibid.*, **66**, 1356 (1944).

(4) P. H. Emmett and S. Brunauer, *ibid.*, **56**, 35 (1934).