Hoffmann and Peters. In those latter foams the foam density gradient can be calculated by means of equation (15), since $A/t_2 = u$ and L_g remains constant.

The relation between Σ and L_g has been tested experimentally. Previous attempts to find an experimental relation between dynamic and static methods have failed[8] because comparable units were not employed. The present analysis makes it clear that in the earlier work Σ (dynamic) was compared to L_l (static) with which it does not necessarily bear any correspondence. In Table VI values of L_g (static) are compared with Σ (dynamic), the latter values being obtained from a dynamic foam meter with a capillary bubbler. As pointed out above, the absolute values of the two units cannot be expected to be the same since the foams are not the same, but it can be seen from the last column in the table that the ratio of the foam stability of the lubricating oil to that of the white oil is comparable in the two systems.

TABLE VI

COMPARISON OF RESULTS OBTAINED BY DYNAMIC AND STATIC METHODS

Liquid used	Unit	Value of unit in c. g. s. at 25°	Ratio
White Oil 1	Σ/ν	6.3×10^{-2}	1.1
Oil A		5.8×10^{-2}	
White Oil 1	$L_g/\nu h_0$	1.56×10^{-3}	1.0
Oil A		1.57×10^{-3}	

Summary

1. A foam meter for the measurement of foam stabilities at different temperatures is described, employing bubbling as the method of producing the foam.

2. Foam stabilities of several types of materials are measured and reported.

3. The static foam units L_f, L_l and L_g are shown to be applicable to different types of material and very different methods of foam measurement.

4. An analysis is made of the various factors that operate in influencing values of L_f, L_l and L_g and the resulting mathematical equations tested by the experimental data here reported.

5. The unit L_g can be converted into a function that expresses the static foam stability of a liquid. For foams of the same character, this function is independent of temperature, viscosity, amount of liquid sample taken, method of producing foam and dimensions of the apparatus.

6. The relation between dynamic and static methods of foam measurement is pointed out.

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[PAPER NO. 110 OF THE LABORATORY OF SURFACE CHEMISTRY, CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND THE UNIVERSAL OIL PRODUCTS COMPANY]

Surfaces of Solids. XI. Determination of the Decrease (π) of Free Surface Energy of a Solid by an Adsorbed Film

BY GEORGE JURA AND WILLIAM D. HARKINS

I. Introduction

The most important effect of the adsorption of a vapor upon a solid is the decrease (π) of free surface energy which accompanies the adsorption. This quantity is, by definition, the film pressure. The value of π is given by the equation

$$\pi = \gamma_S - \gamma_{S_f} = \gamma_0 - \gamma \qquad (1)$$

in which γ_S is the free surface energy of the clean surface of a solid, and γ_{S_f} is the same quantity when the surface is covered by a film. In the more general form of the equation γ_0 represents the free surface energy of any clean surface, and γ that of the surface covered by a film. The free surface energy is the same quantity as the surface tension, which in the case of a liquid may be determined directly, whereas with a solid some other type of experimental method needs to be employed. For this purpose a relationship between the reduction of the free surface energy and some other thermodynamic quantity must be established, and in the case of a solid the simplest of these is the fugacity of a vapor which is adsorbed by the surface of the solid. A method developed on this basis is also applicable to the surface of a liquid, but lacks the simplicity of the direct determination of surface tension.

What is actually involved is the fugacity (f), rather than the pressure, but the two are usually so nearly equal that either may be used. Such equations are applicable to adsorption from solution as well as to that from a vapor phase whenever the fugacity is employed. Examples of the phenomena involved are found (1) in the spreading of (insoluble) stearic acid on water, and (2) in the adsorption of nitrogen on the surface of crystalline TiO_2, and (3) of butyl alcohol from the aqueous phase upon the surface of the water. This paper gives a discussion of the methods used to calculate the lowering of the free surface energy of a solid by an adsorbed film.

II. Theory

Since the change in free surface energy of a solid surface cannot be measured directly, recourse must be taken to some indirect method. Bangham[1,2,3] was the first to show that the reduction of the free surface energy of the surface of the solid could be obtained by the use of the Gibbs adsorption equation. The integration of this equation is expressed by the relation

$$\pi = \gamma_S - \gamma_{S_f} = \frac{RT}{V\Sigma}\int_0^p \frac{v}{p}\,\mathrm{d}p \qquad (2)$$

where R is the gas constant, T the absolute temperature, V the molar volume of gas, Σ the specific area of the solid, p the equilibrium pressure of the adsorbed gas, and v the volume of gas adsorbed per g.$^{-1}$ of solid. This equation has been discussed in a paper from this Laboratory by Boyd and Livingston.[4] However, their numerical results are open to question owing to their method of evaluating the integral, as considered later.

In a series of recent papers, Armbruster[5] and Austin have used the equation in the following form

$$\pi = \frac{RTV_1}{V\Sigma} + \frac{RT}{V\Sigma}\int_{\frac{p}{V}\ \text{as}\ V\to 0}^{\frac{p_1}{V_1}} V\mathrm{d}\ln\frac{p}{V} \qquad (3)$$

The authors attribute this equation to a development of Innes and Rowley.[6] If Eq. 3 is expanded, it is found to be identical with the integration of the Gibbs equation proposed by Bangham. Thus, in actuality, there is only one independent general method of obtaining the decrease in free surface energy of the surface of a solid. Other methods have been proposed.[7] These, however, depend upon an equation of state and cannot be considered suitable for general use.

The numerical evaluation of the integrals in Eqs. 2 and 3 presents certain difficulties. It is obvious that if an equation in v and p were known that would reproduce the isotherm the integrals could be evaluated analytically. Since this is not the case, graphical integration must be used. The greatest difficulty in the computation lies in the low pressure region. In the experience of the writers there is only one procedure which makes it possible to obtain the correct value of the integral. This is to take a large number of experimental points in the very low pressure region. Obviously, the method of measurement in this region must be made more sensitive than that necessary for the remainder of the isotherm. If this is done, it is found that at relative pressures below approximately 0.001 the film behaves like a gas. It is then simple to extrapolate the curve to zero pressure if Eq. 2 is used, or to zero volume if Eq. 3 is used. Frequently, the volume–pressure relationship observed is that of a perfect gas, for which

$$\pi = \frac{RT}{v\Sigma}kp$$

where $k = v/p$. Once the upper limit of existence of this region has been located, the remainder of the computation is simple, regardless of the shape of the isotherm.

Figures 1 and 2 exhibit the curves which need to be integrated when Eqs. 2 and 3, respectively, are used. The curves shown are for the adsorption of n-heptane on TiO_2 (anatase) at 25.0°, whose isotherm is shown in Fig. 5. Obviously the shape of the curve depends on the shape of the iso-

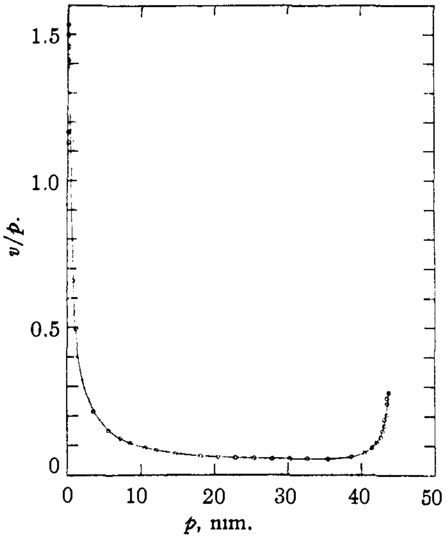

Fig. 1.—Curve for integration of Eq. 2. The total are below the curve up to any point on the curve gives the lowering of the free surface energy (π) at that pressure The curve gives values for the adsorption of n-heptane on anatase.

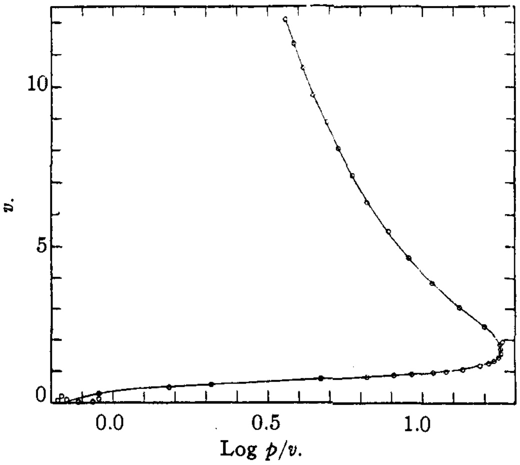

Fig. 2.—Same as Fig. 1, except that it represents the integration of Eq. 3.

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(1) D. H. Bangham, *Trans. Faraday Soc.*, **33**, 805 (1937).

(2) D. H. Bangham and R. I. Razouk, *ibid.*, **33**, 1463 (1937).

(3) D. H. Bangham and R. I. Razouk, *Proc. Roy. Soc.* (London), **A166**, 572 (1938).

(4) G. E. Boyd and H. K. Livingston, THIS JOURNAL, **64**, 2383 (1942).

(5) For example see M. H. A. Armbruster and J. B. Austin, *ibid.*, **66**, 159 (1944).

(6) W. B. Innes and H. H. Rowley, *J. Phys. Chem.*, **45**, 158 (1941).

(7) For example see W. D. Palmer, *Proc. Roy. Soc.* (London), **A160** 254 (1941).

therm. In both cases, the integration must be carried out along the x-axis. An examination of the curves shows that Eq. 3 is simpler to use in the low pressure region, that is up to a relative pressure of about 0.4, whereas Eq. 2 is easier to use beyond this point. Independent integration by each equation, carried out over the entire range for this system, gave values of 39.3 and 39.2 ergs, respectively, per square centimenter at the maximum pressure measured. The values agreed equally well at intermediate points. The scattering of the points for low values of p in Fig. 1 and low values of v in Fig. 2 is within experimental error of the determination of the pressure, and the volume adsorbed in this region.

If the low pressure data are lacking, the only increment of free surface energy which can be calculated is that in the range in which sufficient data have been obtained. The methods of calculation used by Boyd and Livingston[4] gave values which agree with those obtained by the integration of the equation of Brunauer, Emmett and Teller.[8] However this equation, remarkably good over a certain range of pressures, is not at all valid at a relative pressure (p/p_0) below about 0.05. For the adsorption of nitrogen on several solids at a given pressure, the application of the equation gave 18, 17 and 16 ergs per square centimeter, whereas the correct integration gives 29, 23 and 21 ergs per square centimeter, a very large difference between the two methods. This shows that the equation of Brunauer, Emmett and Teller cannot be used for the integration in the *low* pressure region.

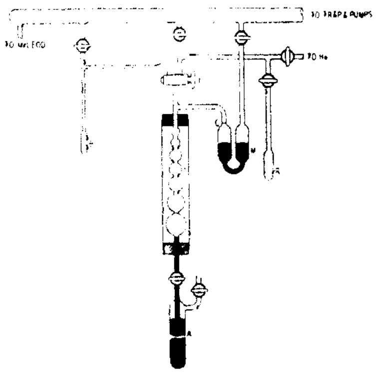

Fig. 3. -Apparatus for the determination of adsorption at pressures below 100 mm.

III. Experimental Procedure

Although the writers have determined the adsorption isotherms of over 200 systems, more than 100 of which have been extended as close to saturation as is feasible, only 6 such systems are considered here, since they illustrate the general relationships sufficiently for our purpose. The non-porous solid chosen for the work is TiO_2 in the form of small crystals of anatase. Adsorption on this solid does not involve capillary condensation. The vapors were those of nitrogen at −195.6°, n-butane at 0.0°, water at 25.0° and **n-heptane**[9] **at 25.0°**. The two other systems employed are those of nitrogen and n-butane on a porous solid.

Materials.—The titanium dioxide was a sample known to be oil free and not surface treated. The crystal structure was investigated by an X-ray analysis. The parameters a_0 and c_0 were both 0.01 Å. lower than those listed by Wyckoff.[10] The nitrogen used was tank nitrogen passed over copper at 500°, a phosphorus pentoxide drying column, and a liquid nitrogen trap to remove any other condensable gases. The water was double distilled, and a second distillation was carried out with acid permanganate present. When freshly prepared, the water had a specific conductance of 10^{-6} ohms^{-1}. The n-butane was obtained from the Riverside Laboratories of the Universal Oil Products Co., where it was twice distilled through a high efficiency fractionating column. The liquid was dried before use. The n-heptane used was Bureau of Standards grade obtained from Westvaco Chlorine Products Co. This liquid was dried over sodium wire for one month and then distilled into a reservoir on the vacuum line.

Procedures.—For the determinations of the isotherms of nitrogen and n-butane at pressures above the gas region, an apparatus similar to that described by Emmett and Brunauer[11] was employed. The apparatus used for the determination of the isotherms of water and n-heptane, and the lower pressure region of n-butane and of nitrogen is represented by Fig. 3. The procedure used with the apparatus and the type of work for which it is suitable are described in the following paragraphs.

The bulb B contains the adsorbent, while R, which holds the liquid whose vapor is to be adsorbed may also be used as a gas reservoir if it is desired to investigate only the very low pressure region of the isotherm. The mercury manometer M is made of 25-mm. tubing, since the diameter should be large in order to allow the meniscus to move freely. A set of calibrated bulbs G is employed to control and measure the volume of the gas adsorbed. A mark C is used in the determination of the volume of that part of the manometer which is in the adsorbing system. Stopcock 1, when open, permits the gas to enter the buret system and then to pass to the adsorption bulb.

The volume of the bulbs in G is determined by the weight of the mercury they hold. Duplicate determinations of the volume of each bulb agree on the average to 0.005 cc. The volume of the left side of the manometer was determined as a function of the distance from the calibration mark to the level of the meniscus, and the volume of the tubing leading from the graduated bulbs was obtained by measuring the change in pressure as the volume in the bulbs is decreased by successively filling them with mercury from the reservoir A. For one system the volume of the tubing was 25.10 cc. The average deviation was 0.02 cc., or less than 0.1%. The dead space in the adsorption chamber was determined with helium, by measuring the initial volume and pressure in the buret system, and also the final pressure after the gas had been allowed to expand into the dead space.

The difference in height of the mercury in the arms of the manometer was determined with a traveling microscope of a sensitivity of 0.001 mm., which was set on a transit mount so that it could be rotated. The average deviation of a given height when a series of readings were taken was found to be 0.002 to 0.003 mm., while that of a single reading from the average did not exceed 0.006 mm. The screw of the microscope was not in error by more than 0.010 mm., and its errors are known to 0.001 mm.

After the surface of the sample has been degassed, the dead space determined, and the sample thermostated, the helium is pumped out, and successive additions of vapor are made. The initial and final volume and pressure of the vapor are measured, and the amount adsorbed is calculated from the gas laws.

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

(9) This determination was made by Mr. Edward Loeser of this Laboratory.

(10) R. W. G. Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, N. Y., 1931, 2nd edition, p. 239.

(11) P. H. Emmett and S. Brunauer, THIS JOURNAL, **56**, 35 (1934).

Figure 4 shows two adsorption isotherms of water vapor on TiO_2 (anatase) as determined by this procedure. The circles are for a determination in which the total adsorbing surface was about 17 m.^{2}, while the squares represent a determination in which about 12 m.^{2} was used. The agreement between the two is excellent. Each of these experiments required about fifty hours to complete.

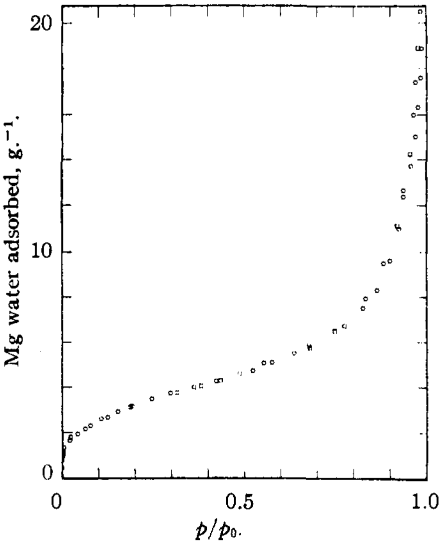

Fig. 4.—Represents two isotherms of water on anatase (TiO_2) as determined independently.

When the isotherm of some condensable liquid, such as water or heptane, is being determined, the work at high relative pressures is very difficult. Here in order to obtain any appreciable increment in the adsorption it is necessary to start with as much volume in the bulbs as possible, and then get the vapor into the adsorption bulb by filling the bulbs with mercury. The compression must be carried out with sufficient slowness so that the pressure of the vapor is kept less than the condensation pressure. Since the rate of adsorption in this region is moderately slow, the compression of the gas must of necessity be slow. It has not been feasible by this method to go to relative pressures above 0.985.

The low pressure at which the adsorption is carried out, when vapors such as those of water or n-heptane are used, permits good measurements on much smaller areas than could be used when the saturation pressure is as high as 700–800 mm. Determinations have been made with apparatus when the total adsorbing surface was only 1 m.^{2}. From the behavior in this case, it appears that moderately accurate isotherms could be obtained with as small an area as 0.25 m.^{2} for the sample in the adsorption chamber.

IV. Results and Discussion

The area of the sample of titanium dioxide used is 13.8 m.^{2}g.$^{-1}$ as determined by our absolute method.[12] The application to adsorption data of the theory of Brunauer, Emmett and Teller gave the following values for the area of the solid: nitrogen, using 16.2 sq. Å. per molecule, 13.9 m.^{2}g.$^{-1}$; water, 10.0 sq. Å. per molecule, 9.4 m.^{2}g.$^{-1}$; n-butane, 38 sq. Å. per molecule, 9.3 m.^{2}g.$^{-1}$; and n-heptane, 45 sq. Å. per molecule, 10.7 m.^{2}g.$^{-1}$.

The area of this solid as determined by our absolute method is 13.8 m.^{2}g.$^{-1}$, and this is the value employed. The area of the porous solid was found to be 128 m.^{2}g.$^{-1}$ as obtained from the nitrogen adsorption isotherm by both the theory of Brunauer, Emmett and Teller on the basis of 16.2 sq. Å. as the area per nitrogen molecule, and the new method developed by the writers.[13]

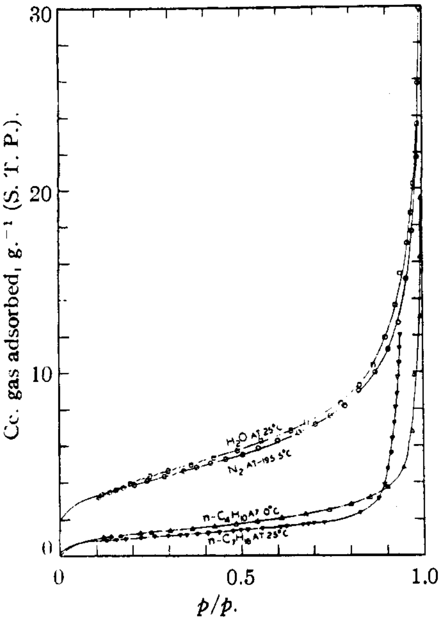

Fig. 5. Adsorption isotherms of water, nitrogen, n-butane, and n-heptane on crystalline TiO_2 (anatase).

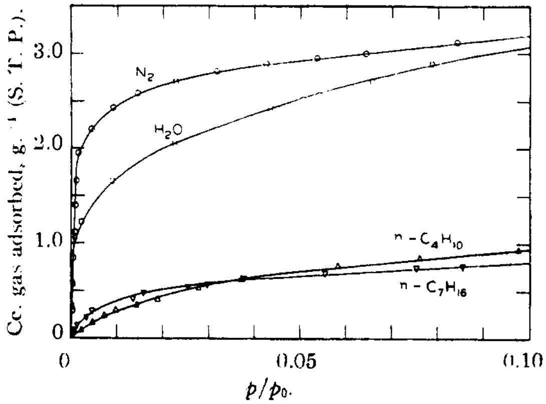

Fig. 6.—Low pressure region of Fig. 5.

The adsorption isotherms of the four gases on titanium dioxide are exhibited in Fig. 5. Fig. 6 shows the same isotherms in detail up to a relative pressure of only 0.10. The adsorption isotherms on a porous solid are represented in Fig. 7, and it is apparent that the low pressure region of the isotherms exhibits the same type of behavior as that of the crystalline anatase. The shapes of the isotherms presented in Figs. 5 to 7 are considered in detail in Paper XIV. With this sample of anatase, the number of molecules of nitrogen and water adsorbed per unit area of surface at a given relative pressure is nearly the same. With

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(12) W. D. Harkins and G. Jura, *J. Chem. Phys.*, **11**, 430 (1943).

(13) W. D. Harkins and G. Jura, *ibid.*, **11**, 433 (1943).

most other solids the water isotherm lies considerably above the nitrogen isotherm.

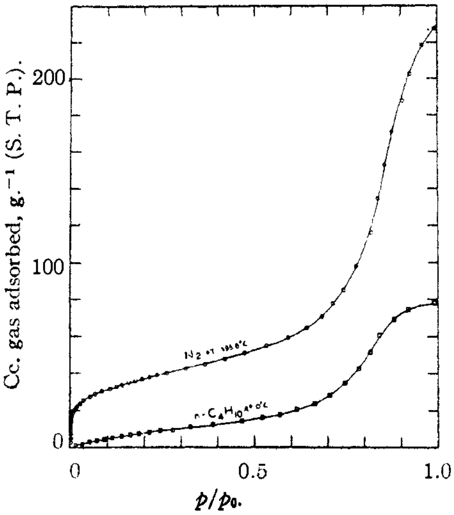

Fig. 7.—Adsorption isotherms for a silica-alumina gel.

V. Variation of Free Surface Energy with Vapor Pressure

It is important to consider the way in which the lowering of free surface energy (π) of a solid varies with the relative pressure of various vapors. As an illustration of the relations, our standard sample of anatase (TiO_2) was chosen, and the amount of the lowering ($\pi = \gamma_S - \gamma_{S_f}$) is given in Fig. 8 for water at 25°, nitrogen at $-195.6°$, *n*-heptane at 25°, and *n*-butane at 0°. The lowering of the free energy (π) decreases in the order in which the vapors are listed. Of these vapors, water effects much the greatest lowering. The factors which establish this order should be considered.

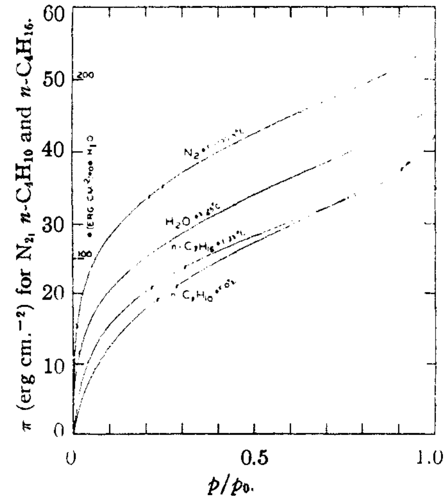

Fig. 8.—Lowering of the free surface energy (film pressure π) for films on anatase as a function of the relative pressure. (Note that values on the Y-axis are four times larger for water than for the other vapors.)

The writers have found that films on solids exhibit the same five phases as oil films on water.[13a] These are: (1) gaseous, (2) expanded, (3) intermediate, (4) and (5), both condensed.

Now, if at any given relative pressure (π) the same surface phase is involved, if the phase transitions of this phase occur at about the same pressures, and if the *p–v* isotherms have about the same shape, then the increase in film pressure (π) increases (1) with decrease in area of the cross section of the molecule parallel to the surface, and (2) is proportional to the absolute temperature.

Similar curves for nitrogen and *n*-butane on a porous polar solid of an area of 128 m.^{2}g.$^{-1}$ are given in Fig. 9. These exhibit two points of inflection, the upper one of which is less evident for this particular material than with other porous solids of this type. However, the non-porous powder exhibits only one point of inflection. The nitrogen film represented in this figure, with increasing pressure exhibits the phases (1) gaseous, (2) condensed and (3) a second condensed phase, while with *n*-butane, the phases are (1) gaseous, (2) expanded and (3) intermediate. In contrast, the films on the crystalline solid exhibit *in every case* a condensed film in the middle region of pressures.

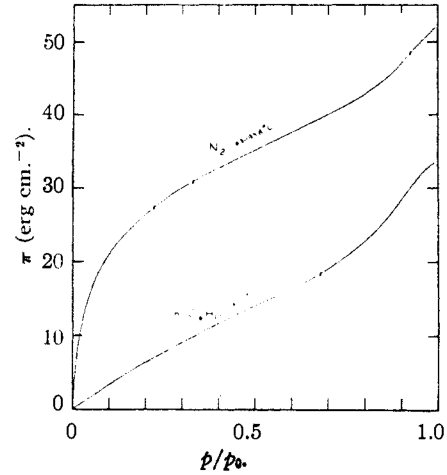

Fig. 9.—Values of π for films on a porous silica-alumina gel.

The flattening of these curves for the porous solid at the highest pressures is due to the fact that the pores of the solid are progressively filled

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[13a] The method employed is described in Paper XIV of this series. Each of the five phases of oil films on water exhibits a relation between film pressure (π) and molecular area (σ) which is characteristic of that phase and that phase alone. Whenever the data for an adsorbed film on a solid fit the equation for a particular phase over a sufficiently large variation in π or σ, the phase is designated as that for which the equation is characteristic. For example the relation for a condensed oil film on water is

$$\pi = b - a\sigma$$

so if this equation represents accurately the data for a film on a solid, this film is also designated as condensed. For the other phases the equations are more complicated, but the agreement between the data and each equation is also excellent.

with the adsorbate, thus reducing the available adsorbing area. Thus the value of the reduction of the free energy per unit area becomes questionable when it is applied to porous materials at high relative pressures, *i. e.* in this particular case, at values of p/p_0 of around 0.8 or greater. No general statement can be made concerning the exact relative pressure at which this effect becomes important.

The values of (π) thus far found with different polar solids, both non-porous and porous, fall between the following limits in erg cm.$^{-2}$: water at 25°, 180 to 250; nitrogen at −195.8°, 35 to 56; *n*-butane at 0°, 30 to 45; *n*-heptane at 25°, 37 to 44. Preliminary work with rutile indicates that the value with nitrogen is about 10 to 15 erg cm.$^{-2}$ higher than the maximum given above. According to the theory already developed,[14] water on a hydrophobic solid such as graphite cannot exhibit a film pressure higher than the surface tension of water (72 dyne cm.$^{-1}$ at 25°). Oil films on water usually collapse at pressures (π) below 50 dyne cm.$^{-1}$, but the film pressure rarely may attain values of the order of 60 dyne cm.$^{-1}$.

In the present investigation an interesting relationship was found. With nitrogen, the lower the relative pressure at which the monolayer is completed as calculated by the theory of Brunauer, Emmett and Teller, the greater the reduction of the free surface energy at this point. Figure 10 shows the relationship between the reduction in free energy when the monolayer is completed, and the relative vapor pressure required to complete the monolayer. Other gases seem to exhibit the same relationship, but the data are not sufficiently extensive to make this certain.

A knowledge of the lowering of the free surface energy (π) by an adsorbed film on the surface of a solid is important as a basis for the calculation of other fundamental magnitudes. Thus it has been shown[14] that the work of adhesion between a liquid and a solid is given by the relation

$$w_A = \pi_e + \gamma_L (1 + \cos \Theta)$$

which, in the case of a zero contact angle, reduces to

$$w_A = \pi_e + 2\gamma_L = \gamma_S - \gamma_{SL} + \gamma_L$$

where π_e is the lowering of the free surface energy of the solid in equilibrium with the saturated vapor of the liquid.

Corresponding equations for the free energy of emersion of a clean solid from a liquid are

$$f_E = \pi_e + \gamma_L \cos \Theta \text{ and } f_E = \pi_e + \gamma_L = \gamma_S - \gamma_{SL}$$

The spreading coefficient of the liquid on the clean solid is given by the equation

$$S_{L/S} = \pi_e = \gamma_S - \gamma_{SL} - \gamma_L$$

The magnitudes of a few of these important quantities, as calculated by the method presented in this paper, are presented in Table I. The work of adhesion between anatase and water is very much higher than between this solid and nitrogen, or normal butane or heptane. It may be noted that, even although the values are for unit area, the larger hydrocarbon molecules of heptane give a larger work of adhesion than the smaller molecules of butane.

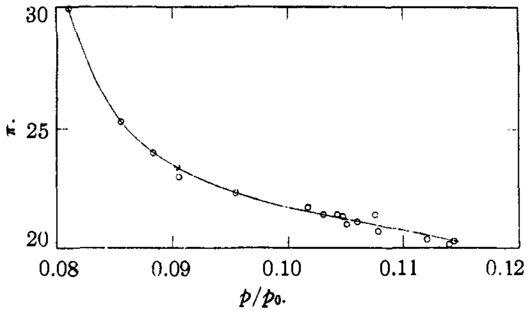

Fig. 10.—Values of the lowering of the free surface energy (π) on completion of a monolayer of nitrogen (as calculated by the theory of Brunauer, Emmett and Teller) and the relative pressure (p/p_0) of the nitrogen at that point.

TABLE I

WORK OF ADHESION, SPREADING COEFFICIENT AND FREE ENERGY OF EMERSION BETWEEN TiO_2 (ANATASE) AND VARIOUS LIQUIDS (ERG CM.$^{-2}$)

Liquid	Spreading coefficient $S_{L/S} = \pi_e = \gamma_S - \gamma_{SL} - \gamma_L$	Free energy of emersion $f_E = \gamma_S - \gamma_{SL}$	Work of adhesion $w_A = \gamma_S - \gamma_{SL} + \gamma_L$
H_2O	190	262	334
N_2	56	64	72
n-C_4H_{10}	43	58	73
n-C_7H_{16}	46	66	86

In the present series of papers, however, the prime interest in the lowering of the free surface energy of the solid lies in the calculation of the pressure (π)–area (σ) isotherms of the films of the adsorbed gases on the surface of the solid as shown in Figs. 8 and 9 and much more extensively in Paper XIV. It is interesting that *all* the phases known for insoluble films on water are present. The complete discussion of these figures is reserved for a paper, XIV, where it is shown that the films of adsorbed gases on solids give the same π–σ relationships as insoluble films on water.

Summary

1. In order to obtain the lowering (π) of the free surface energy (γ_S) of the surface of a solid caused by the presence of a film adsorbed from a vapor, it is necessary to obtain a considerable number of experimental data which give the pressure of the vapor and the amount of vapor adsorbed when the temperature is constant. The method used is to integrate the isotherm by use of the relation

$$\pi = \gamma_S - \gamma_{S_f} = \frac{RT}{V\Sigma} \int_0^p \frac{v}{p} dp$$

or an equivalent relation used later by Armbruster.

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[14] W. D. Harkins and H. K. Livingston, *J. Chem. Phys.*, **10**, 42 (1942).

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.

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

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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 described 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