[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CHICAGO AND THE UNIVERSAL OIL PRODUCTS COMPANY]

Surface of Solids. X. Extension of the Attractive Energy of a Solid into an Adjacent Liquid or Film, the Decrease of Energy with Distance, and the Thickness of Films

BY WILLIAM D. HARKINS AND GEORGE JURA

1. Introduction: Heats of Adsorption.—A fundamentally important, entirely unsolved problem of physics and chemistry, is that of the distance to which the attractive field from a solid has an effect upon the energy of molecular interaction with an adjacent liquid or film. The solution of this problem involves a determination of the variation of the intermolecular energy with the distance. This paper presents an experimental, though difficult, method by means of which the problem may be solved, together with experimental data for a single case, that of water on titanium dioxide in the form of pure anatase. From earlier results obtained in this Laboratory, many other solids should exhibit the same general relationship between energy and distance.

Although calculations have been made of the heats of adsorption of gases on ionic crystals,[1] on metals,[2] and on graphite,[3] no calculation, which is even approximately correct, has been made of the variation of the attractive energy with the distance.

2. Theories of Adsorption.—For many years there have been two contradictory theories of the ultimate thickness of adsorbed films on a solid subphase: (1) the *monomolecular* theory, the principal exponent of which is Langmuir, and (2) the *polymolecular* theory.[3a] The latter theory does not assume that all adsorbed films are polymolecular, since it is evident that films of water on paraffin, graphite, talc and other hydrophobic solids may be monomolecular even at values of p/p_0 nearly as high as unity. Indeed it seems possible in such cases that even at saturation, the film is either monomolecular, or, if a second layer is formed, it is far from completely filled. However, *evidence* which indicates the existence of adsorbed monolayers on *non-porous solids at high values of p/p_0 is almost non-existent,* since there seems to be not *more than a single known isotherm for a non-porous solid,* that of propyl alcohol on barium sulfate, which indicates a film that remains almost monomolecular up to pressures as high as $p/p_0 = 0.95$. Presumably this is due to some extent to the neglect by investigators of systems of this type. This isotherm is discussed later (Section 6). Langmuir's recent statement[4] of the monomolecular nature of films is, that for films of argon, nitrogen, hydrogen, and methane, at liquid air temperatures "the amount adsorbed increases about in proportion to the pressure, but at higher pressures reaches a limiting value which in every case studied corresponds to less than a monolayer. Evidently, therefore, even with these cases of adsorption which involve merely van der Waals forces, the effective range of action of the forces responsible for the adsorption is less than the molecular diameter, so that we are still clearly dealing with forces which act between atoms or molecules in contact."

Many other investigators have adopted this general point of view, as expressed by Langmuir's adsorption isotherm.[5]

A theory which gives an isotherm which indicates polymolecular adsorption, has been developed by Brunauer, Emmett and Teller[6] (BET) on the basis of the earlier work of Emmett and Brunauer.[7] This isotherm has proved to be remarkably successful and will be discussed in a later paper of this series.

3. Variation of the Attractive Energy with Distance: Thermodynamic Theory and Experimental Method.—We will first consider a sample of a crystalline powder which exhibits an area of 1 sq. cm. The surface of the solid (quartz, TiO_2, $BaSO_4$, $ZrSiO_4$, etc.) is made clean by outgassing at as elevated a temperature as can be employed without affecting the nature of the surface. During this operation the powder is in the tube H of Fig. 1. The apparatus is now placed in a thermostat and after thermal equilibrium is attained, the tip of the small glass tube T is broken. This tube contains a small amount of water whose weight is determined on a microbalance. In different experiments the amounts of liquid are so chosen that the final vapor pressures of the adsorbed films at equilibrium cover well the range from $p = 0$ (no liquid) to $p/p_0 = 1$.

A calorimeter (Fig. 2) which contains n' moles of liquid is used for the measurements of energy. A 36-junction copper–constantan thermel with a sensitivity of 2×10^{-5}° was employed. For the sake of simplicity the equations are developed for an amount of powder which has an area of 1 sq. cm. The processes (Fig. 3) are as follows:

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(1) F. V. Lenel, *Z. physik. Chem.*, **B22**, 379 (1933); W. J. C. Orr, *Trans. Faraday Soc.*, **35**, 1247 (1939); *Proc. Roy. Soc.* (London), **A173**, 349 (1939).

(2) J. E. Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932); Bardeen, *J. Phys. Rev.*, **58**, 727 (1940); H. Margenau and W. G. Pollard, *Phys. Rev.*, **60**, 128 (1941).

(3) R. M. Barrer, *Proc. Roy. Soc.* (London), **A161**, 476 (1937).

(3a) The prefixes mono- and poly- are adopted on account of prevalent usage, and not from their etymological suitability.

(4) I. Langmuir, *J. Chem. Soc.*, 511 (1940).

(5) I. Langmuir, THIS JOURNAL, **40**, 1361 (1918).

(6) S. Brunauer, R. H. Emmett, and E. Teller, *ibid.*, **60**, 309 (1938).

(7) For references to these and other papers on adsorption, see S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943.

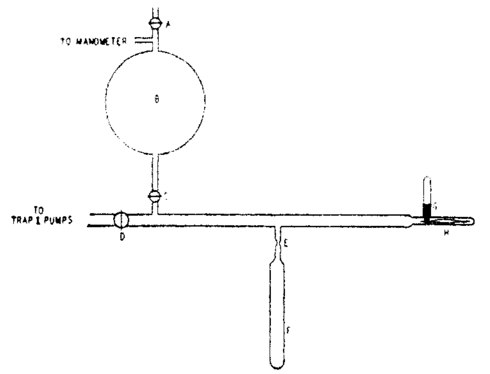

Fig. 1.—Simplified diagram of apparatus for the adsorption of water vapor on a finely divided crystalline solid in *six* bulbs (F). The water is weighed in the tube H before adsorption and adsorbed on the solid in the bulbs. G is a piece of soft iron used for breaking off the point of the tube H, and B is a gas filled bulb used for the determination of the free volume of the remainder of the apparatus up to the stopcocks C and D.

first step, the powder, with an area of 1 sq. cm., on which area n moles of liquid has been adsorbed at a value of $p/p_0 \leqq 1$, is immersed in the liquid. The change (ΔH) in the value of the Gibbs heat function (enthalpy) which accompanies this proccess is:

$$\Delta H_1 = -h_{E(S_fL)} \quad (1)$$

where E indicates the process of emersion, which is the opposite of immersion, h indicates the increase in the value of enthalpy per unit area, and $E_{(S_fL)}$ indicates the emersion of the solid, covered by its film, from the liquid. Second step: since by the actual process (immersion) n moles of liquid have been added to the n' moles initially present, this amount of n moles is now evaporated from the liquid. Now for this step

$$\Delta H_2 = n\lambda \quad (2)$$

where λ is the molar latent heat of vaporization of the liquid. Third step: the sample of powder is now emersed from the liquid into a vacuum, carrying no film with it, so

$$\Delta H_1 = h_{E(SL)} \quad (3)$$

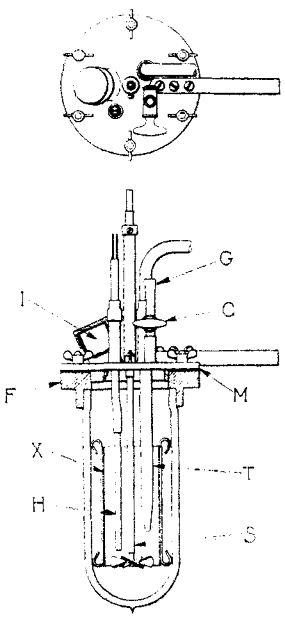

Fig. 2.—Calorimeter. T, 36-junction thermel; H, heating element; G, inlet for liquid; C, stopcock; X, chimney to give better circulation of powder; I, opening for introduction of powder. For non-aqueous liquids the calorimeter used is shown by Boyd and Harkins, THIS JOURNAL, **64**, 1191 (1942).

It is obvious that this process must be carried out in the reverse direction, *i. e.*, by immersion instead of emersion, so $q_{I(SL)} = h_{E(SL)}$, where $q_{I(SL)}$ is the heat evolved in the process of immersion.

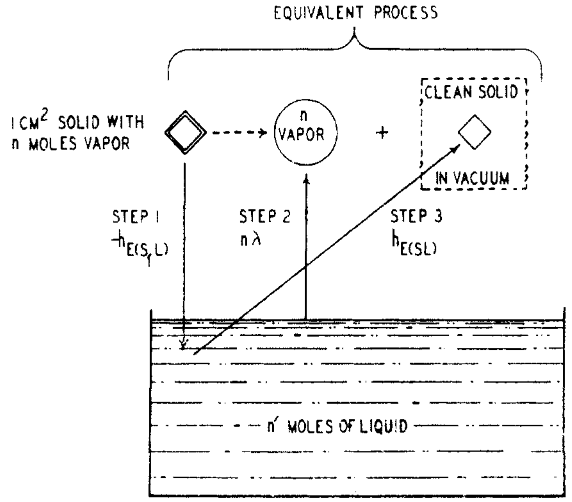

Fig. 3.—Steps 1, 2 and 3, by means of which a solid with an area of 1 sq. cm., with n moles adsorbed on the surface, is transformed into n moles of vapor and the solid in a vacuum. The equivalent process involves merely the desorption of the n moles from the surface.

As the effect of the summation of these three processes the solid of area 1 sq. cm., covered by a film of n moles in equilibrium with vapor at a pressure p, is converted into the solid with a clean surface and n moles of vapor. Thus the complete process corresponds to the desorption of n moles of vapor from 1 sq. cm. of surface of the solid, so the increase of enthalpy on desorption [$h_{D(VS_f)}$] is given by the summation of the three terms or

$$h_{D(VS_f)} = h_{E(SL)} - h_{E(S_fL)} + n\lambda \quad (4)$$

Now

$$h_{E(SL)} = h_S - h_{SL} \quad (5)$$

and

$$h_{E(S_fL)} = h_{S_f} - h_{SL} \quad (6)$$

Substitute (5) and (6) in (4), which gives

$$h_{D(VS_f)} = h_S - h_{S_f} + n\lambda \quad (7)$$

Now, since in general if γ represents the free surface energy

$$h = \gamma - T(\partial\gamma/\partial T)_{p,\Sigma} \quad (8)$$

$$h_{D(VS_f)} = \gamma_S - \gamma_{S_f} - T\left(\frac{\partial\gamma_S}{\partial T} - \frac{\partial\gamma_{S_f}}{\partial T}\right)_{p,\Sigma} + n\lambda \quad (9)$$

In cal. g.$^{-1}$ Eq. 7 may be written

$$H_{D(VS_f)} = H_{E(SL)} - H_{E(S_fL)} + n'\lambda \quad (10)$$

where n' is now the number of moles adsorbed per gram. $H_{E(SL)}$ is the heat of emersion of the clean powder from the liquid in cal. g.$^{-1}$, and $H_{E(S_fL)}$ is that for 1 g. of solid on whose surface n' moles of vapor has been adsorbed. In cal. mole^{-1}

$$H_{D(VS_f)} = \frac{1}{n'}\left[H_{E(SL)} - H_{E(S_fL)}\right] + \lambda \quad (11)$$

These equations are applicable to porous as well as non-porous solids.

The relationship used *universally* in the literature *is incorrect*, even though it is believed to be applicable only at saturation

$$H_{D(VS_f)} = H_{E(SL)} + n'\lambda \qquad (A)$$

For example, the correct equation applied to the data of Razouk[8] gives a heat of adsorption (q_a) of 9.9 cal. g.$^{-1}$ for methyl alcohol on charcoal at 13.5% of saturation, while the *incorrect* equation (A) gives $q_a = 22.4$ cal. g.$^{-1}$.

γ free surface energy
γ_S the free surface energy of the clean solid (ergs cm.$^{-2}$)
γ_{S_f} the free surface energy of the solid with adsorbed film
λ heat of vaporization (cal. mole^{-1})
Σ area

4. Variation of Energy of Interaction with Distance from the Surface of the Solid.—For the experimental work a sample of pure non-porous titanium dioxide in the form of anatase was used. This is oil free, not surface treated, and its cell constants have been determined as a = 3.77 Å. and c = 9.49 Å. while Wyckoff gives a = 3.78 Å. and c = 9.50 Å. A part of this same sample was photographed by the use of an electron microscope (Fig. 4).

The area of this sample is 13.8 m.^{2}g.$^{-1}$ as determined by our absolute method. This consists in adsorbing a duplex film of water on the surface in saturated water vapor, and then immersing in water in the calorimeter. The heat developed, expressed in ergs, when divided by 118.5 erg cm.$^{-2}$, the surface energy of water at the temperature employed, gives the area of the powder. A very small correction is made for the known thickness of the duplex film. The area of this same sample when calculated by the use of the isotherm of Brunauer, Emmett and Teller,[8] and of Emmett's value of 16.2 sq. Å. for the mean area of the nitrogen molecule, is 13.9 m.^{2}g.$^{-1}$, or a difference of less than 1% between the results of the two methods.

The isotherms of water on this anatase at 25° and of nitrogen at −195.6° are exhibited in Fig. 5, while Fig. 6 and Table I give the relationship between the energy of emersion of the solid from water at 25°, and the amount of water left on the surface of the solid. For the emersion of the dry solid the energy is 512 erg cm.$^{-2}$.

The relationship between the energy of desorption of water to give a dry surface, with the number of moles per sq. cm., is exhibited in Fig. 7, as calculated by Equation 4, while Figure 8 gives values for the molal heat of desorption of the vapor as a function of the weight of water adsorbed.

These figures give in addition the thickness (T) of the films in Å. These are calculated on the basis of the assumption that the *mean density* of the film is the same as that of the three dimen-

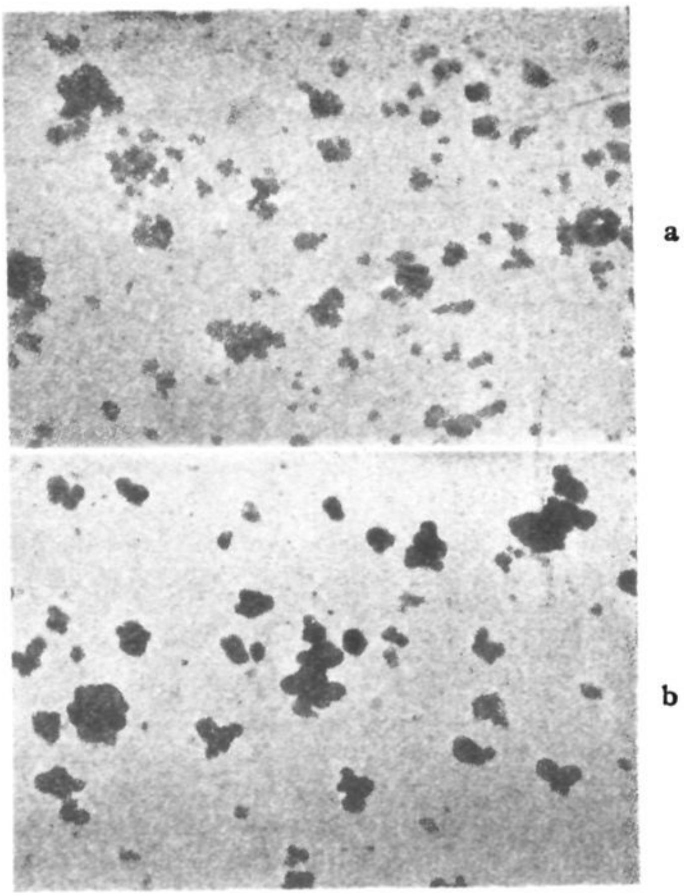

Fig. 4.—(a) Electron microscope photograph (×14,600) of a TiO$_2$ (anatase) powder of area 13.8 sq. m.g.$^{-1}$ by our absolute method, and 13.9 sq. m.g.$^{-1}$ by the method of Brunauer, Emmett and Teller on the basis of the assumption that the mean area per N$_2$ molecule is 16.2 Å.^{2} (Emmett). (b) The same (×14,600) for TiO$_2$ of area 8.7 sq. m.g.$^{-1}$. (Photographs by E. F. Fullam, Interchemical Corporation.)

TABLE I

ENERGY OF EMERSION OF TITANIUM DIOXIDE (ANATASE) FROM WATER AT 25° AS A FUNCTION OF THE THICKNESS OF THE WATER FILM WITH WHICH IT EMERGES

1 mg. H$_2$O g.$^{-1}$ in film	2 Mean thickness[a] of film in Å., T	3 Energy of erg cm.$^{-2}$ $h_{E(S_fL)}$
0	0	512[a]
0.548	0.4	399
0.953	0.7	366
1.68	1.2	289
1.99	1.4	279
2.60	1.9	210
3.15	2.3	190
3.68	2.7	172
4.95	3.6	142
5.86	4.2	139
8.66	6.3	127
11.86	8.6	125
14.20	10.0	122
Saturated	>15.0	119

[a] $h_{E(SL)}$.

(1) This was determined by weighing the solid before and after adsorption.

(2) The mass obtained in (1) is divided by the density of the liquid, which gives the volume the film would have in the uncompressed state. The volume (V) divided by the area (Σ) of the solid gives T the thickness.

(3) This is the quantity of heat developed by immersion of the solid in water in the calorimeter, divided by the area (Σ).

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

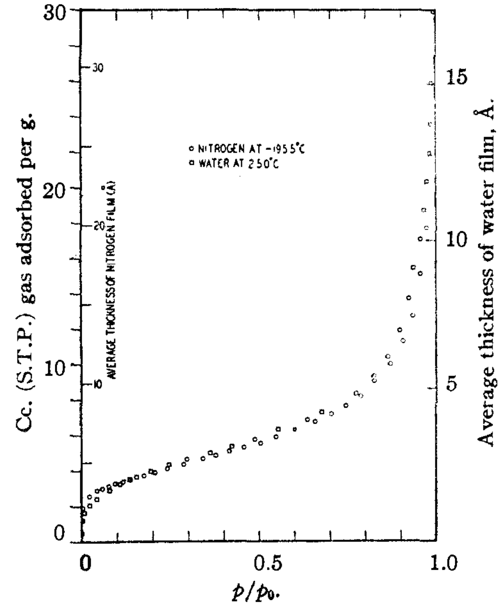

Fig. 5.—Isotherms of nitrogen at −195.8° and water at 25°. The number of molecules adsorbed at any (not too high) given value of p/p_0 is practically the same. However the nitrogen molecules are larger than those of water, so the nitrogen films are thicker (see graph) than those of water. At saturation the nitrogen film is much thicker.

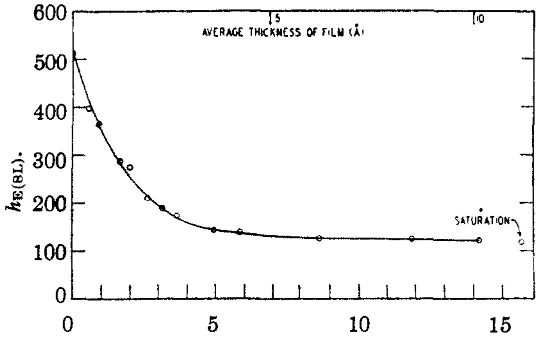

Fig. 6.—Thickness of the water film and the energy of emersion per sq. cm. of the surface of TiO_2 (anatase). The weight of water adsorbed per gram of anatase is also given.

sional liquid at the same temperature. Obviously this cannot be quite correct, but it should become more nearly correct as the film thickens. There is also involved the assumption that the thickness is uniform over the whole surface. The mass of the film was determined by *weighing* in all cases in which the energy was determined. The total amount of water adsorbed is sufficient to allow this to be done.

Figure 5 indicates that at saturation at 25°, the thickness of the adsorbed water film is somewhat greater than 15 Å., (or 5 molecules of water) since it has this thickness at the last point which represents a pressure below saturation. The amounts of water adsorbed for this isotherm were calculated from the volume of vapor.

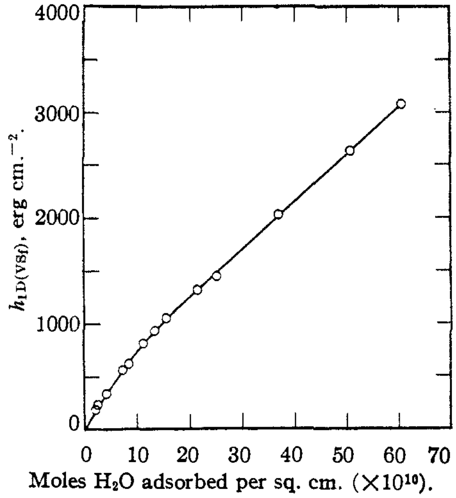

Fig. 7.—Variation of the energy of emersion per sq. cm. of area of TiO_2 (anatase) with the weight of water vapor adsorbed.

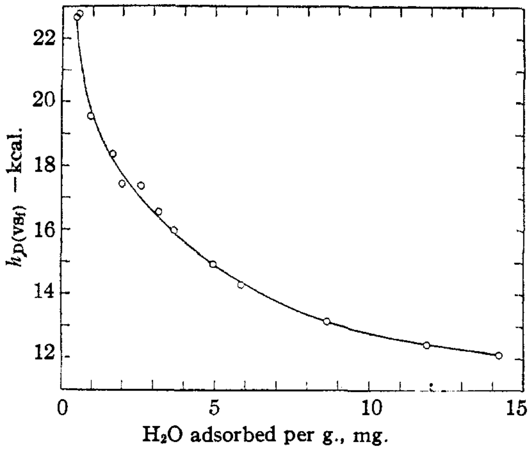

Fig. 8.—Decrease in the energy of desorption, in calories per mole of water, from the surface of TiO_2 (anatase) as a function of the weight of water adsorbed.

5. Variation of the Energy of Desorption with the Number of Molecular Layers.—It is of interest to estimate the variation of the molar energy of desorption with increase in the number of molecular layers (Table II).

The increase in the energy of vaporization of water by the presence of the adjacent solid is given in column 4. Thus the vaporization of the first molecular layer requires 6550, the second 1380, and the third 450 cal. mole^{-1} more energy to vaporize than if water alone were present. Thus these values give the increase in molecular interaction due to the presence of the solid.

The theory of Brunauer, Emmett and Teller was used to calculate the number (N) of molecules in the monolayer (1) next to the surface of the solid. It was assumed as the basis of the cal-

TABLE II

MOLAR ENERGY OF DESORPTION OF MOLECULAR LAYERS OF WATER FROM THE SURFACE OF TITANIUM DIOXIDE (ANATASE)

1 Number of layer	2 Internal energy of desorption, cal. mole^{-1}, $H_D(v_nS)$	3 Internal energy of vaporization of water, λ_l	4 $H_D(v_nS) - \lambda_l$ or $E_n - E_L$ determined	5 Theory of exponential decay
1	16450	9900	6550[a]	6550
2	11280	9900	1380	1637
3	10350	9900	450	409
4	9980	9900	80	102
5	9940	9900	40 (?)	26
Sum of all above 5			30 (?)	

Column 2 gives the energy of desorption for a whole layer, when all of the lower layers are complete.

Column 3 gives the internal energy of vaporization which does not include the work done.

[a] The BET theory gives a value for E_1-E_L of 2100 cal. mole^{-1}.

culation that the number of molecules in each higher layer is also equal to N. The values obtained by the application of this theory indicate that the water molecules in the first layer (1) are somewhat loosely packed, at 25°, while at $-195.8°$ nitrogen molecules (which are larger) are more nearly in contact.

The values of column 4 suggest an exponential decay in the energy of desorption. In column 5 it is assumed that the value of 6550 cal. mole^{-1}, as given in column 4 is correct, and that the energy for any other layer is one-fourth of that of the layer just beneath it. In *general* this gives the same rate of decay as that exhibited by the experimental values but it may be noted that these latter are lower for even layers and higher for odd layers, than corresponds to the exponential decay. This is just what would be expected if the more polar part of the water molecules is turned toward the solid in the first layer, away from it in the second, toward it in the third, etc. This is exactly the type of orientation exhibited in built-up multilayers of polar–non-polar molecules. Unfortunately, the values of column 4 do not have sufficient accuracy to prove that this alternation in orientation actually occurs.

6. Discussion: Polymolecular Films.—The important relation brought out in Section 4 is that for water on a non-porous crystalline "polar" solid (anatase) the attractive energy exhibits an essentially exponential decay. The term "polar" solid is used because a better term has not, as yet, been introduced. The term is used to designate solids, such as quartz, etc., whose molecular interactions may be considered to exhibit not too small *relative* intensities of both dispersion forces and those due to segregated electrical charges, in addition to repulsive forces. On such solids the curve which represents the decrement ($-\Delta\gamma = \Delta\pi$) of free surface energy due to a film of nitrogen at $-195.8°$ has the same form (with smaller magnitudes) as that for water at 0°. The film of nitrogen attains, very slightly *below* saturation, a thickness of 36 Å., while for water, as cited earlier, the value is 15 Å. On the whole it does not seem improbable that nitrogen, a non-polar adsorbate, also may exhibit an essentially exponential decay of the attractive energy.

The saturated film of butane at 0° on this same solid, is 64 Å. thick, so it is not essential to use a polar adsorbate in order to have a highly polymolecular film. However, it is true that the butane molecule has a high polarizability. While the water film attains a thickness of about 5, and that of nitrogen about 10 molecular layers, the number for butane cannot be specified, since in its first monolayer *the molecules lie flat*, while near the outer surface of the film they must have much more nearly the type of orientation exhibited by the surface of liquid butane. If the thickness of this film is to be specified in molecules as units all that can be said is that its thickness is of the same general order as that of nitrogen (10 molecules).

It is of interest to note in connection with the discussion of the two preceding paragraphs, that with the particular sample of titanium dioxide used for this work the adsorption isotherms for nitrogen at $-195.6°$ and water at 25° are practically identical except possibly very close to saturation, both in form and the volume of gas adsorbed (Fig. 5).

Thus the writers have obtained entirely definite evidence that adsorbed films of water, nitrogen, and butane on titanium dioxide in the form of anatase are highly polymolecular, with *thicknesses* of 15, 36 and 64 Å., respectively, at pressures just below saturation. We believe that these are correct thicknesses for pressures *very* slightly below saturation, except that the thickness of the water film may be greater than 15 Å. As has been specified these values express the volume of the liquid at the given temperature divided by the area, as determined by the area of the surface of the solid. If the film has a density higher than the three dimensional liquid, then these values in actual ångström units are that much too high, but in terms of molecular diameters the values are not affected.

No uncertainty is introduced by the value of the area which is employed for the calculation, since the determination of area was made by our absolute method. This method is based upon the premise that water on anatase forms a film sufficiently thick to be *duplex*, *i. e.*, the surface of the film is sufficiently thick to give inappreciable (experimentally) interaction between the outermost layer of the film and the solid. Thus the surface energy of the outer part of the film is supposed to be the same as that of water at the same temperature. That this is true within the limits of experimental error is shown by the fact that as the thicker films thicken there is no detectable decrease in the energy of immersion. Thus, for the first time, certain evidence has been obtained for the highly polymolecular character of certain adsorbed films. As mentioned earlier, no attempt is made here to prove the *non-existence* of monomolecular adsorbed films at high values of p/p_0 that are less than unity.

Monomolecular films of stearic acid are formed by adsorption of the acid at the interface between *dry* benzene and TiO_2 (anatase) such as that used in this investigation. In fact, even the monolayer is loosely packed, since only about 70% as much stearic acid is adsorbed as the amount required for close packing.

The writers have considered it important to obtain *definite* evidence, already presented in this paper, which shows that by the adsorption process alone films taken up from vapors on the surfaces of solids become highly polymolecular at the higher values of p/p_0, provided the contact angle between the solid and the liquid is zero. That this point of view is not universal among specialists in the field of adsorption, is shown by a recent statement by Brunauer,[9] who is, himself, an enthusiastic supporter of the theory of polymolecular (multimolecular) adsorption:

"Many advocates of the capillary condensation theory maintain that adsorption in porous bodies is largely due to capillary condensation, although they do not deny the existence of unimolecular adsorption. The two schools (unimolecular and capillary condensation) of thought meet on a common ground, namely, that adsorption on a plane surface where capillaries do not exist must be unimolecular."

Since Langmuir is the principal advocate of the uni- or mono-molecular theory, it is important to consider his point of view, as presented in the following quotations[10]:

"The theory requires that in typical cases of true adsorption the adsorbed film should not exceed one molecule in thickness. This is contrary to the usual viewpoint. The discrepancy is accounted for by the fact that nearly all investigators have worked with porous bodies in which the adsorbing surface is indeterminate, or have used nearly saturated vapors so that condensation of liquid occurred in capillary spaces. Others have mistaken solution or *ab*sorption for adsorption.

"With gases or vapors at pressures much below saturation the surface of a solid tends to become covered with a single layer of molecules. The reason for this is that the forces holding gas molecules (or atoms) on to the surface of solids are generally much stronger than those acting between one layer of gas molecules and the next. When the vapor becomes nearly saturated, however, the rate of evaporation from the second layer of molecules is comparable with the rate of condensation so that the thickness of the film may exceed that of one molecule."

Since the experiments of the authors and of others show that most of the known films on *non-porous* solids are polymolecular at values of p/p_0 greater than 0.3 or less, the above conception of Langmuir cannot be used as the basis of *any* general theory of adsorption.

Capillary Condensation Theory.—The monomolecular theory of adsorption on solids receives support at the present time only because the apparent discrepancies which it introduces are explained away by the theory of capillary *condensation*. Undoubtedly this phenomenon is prominent in highly porous solids, but it does not contribute as much to the "sorption" as is assumed by the adherents of this theory.

Indeed, at high relative pressures, the total amount adsorbed is commonly *greater per unit area on a plane surface*, where the high value cannot be explained by the assumption of capillary condensation, *than the total amount of "sorption" for the same area exhibited by a porous solid*. The explanation of this fact is simple: the adsorption in pores is limited by the growth of the film from all sides of the pore. In the simple case of a pore with parallel plane walls the "film" cannot be thicker than half the distance between the walls. When the values for the thicknesses of films of water, nitrogen, and butane given in this paper are considered, it is evident that many of the smaller pores in a silica gel or a catalyst of high area, would become completely filled by adsorption even if capillary condensation were absent.

That capillary condensation, as suggested by Zsigmondy,[11] plays an important part in the sorption, is undoubtedly true. However, the assumption by others than Zsigmondy that this phenomenon is responsible for all of the material taken up from a vapor by a porous body, with the exception of a single monolayer, is certainly false. If this assumption had not been made, the monomolecular theory of adsorption could not have survived up to the present time.

7. Monomolecular and Slightly Thicker Films on Solids.—It is shown earlier in this paper that almost all of the films on non-porous solids thus far investigated begin to lose their monomolecular character at a relatively small value of p/p_0 which is of the order of 0.08 to 0.12 for nitrogen at −195.6° and of 0.15 to 0.25 for *n*-butane at 0° and for water at 25°.

If it is desired to find a film which remains in the monomolecular state up to high values of p/p_0 when adsorbed on a polar solid, it would seem that the choice of a substance whose molecules are polar–non-polar, would be a good one. Thus molecules of an alcohol should, in the first

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[9] S. Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Physical Adsorption, Princeton University Press, Princeton, N. J., 1942.

[10] I. Langmuir, THIS JOURNAL, **40**, 1401 (1918), also *J. Chem. Soc.*, 511 (1940).

[11] R. Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911).

monolayer, be oriented with their long axis perpendicular to the surface of a polar solid and with the polar group toward the solid. This leaves the hydrocarbon chains, which resemble paraffin, and which exhibit little attractive energy, on the outside. It would seem that this would give a good chance of obtaining a film which remains monomolecular up to high values of p/p_0. However, the presence of the polar group makes the position of the molecule highly dependent on the surface lattice of the crystal used for adsorption, which should on this account give variations in the thickness of the adsorbed film.

As mentioned earlier (Section 2) the only system which the writers know, that exhibits monomolecular adsorption on a non-porous solid, is propyl alcohol on barium sulfate. The area available per molecule of the alcohol, and the mean thickness of the films are given in Table III as a function of the relative vapor pressure (p/p_0).

TABLE III

PROPYL ALCOHOL FILMS; MONOMOLECULAR ON BARIUM SULFATE UP TO $p/p_0 = 0.9$; DO NOT COMPLETE THEIR SECOND LAYER ON TiO_2 AT $p/p_0 = 0.8$, AND COMPLETE THEIR SECOND LAYER ON QUARTZ AT $p/p_0 = 0.7$.

	$BaSO_4$		TiO_2 (Anatase)		SiO_2 (Quartz)	
p/p_0	Area per molecule, $Å.^2$	Film thickness, Å.	Area per molecule, $Å.^2$	Film thickness, Å.	Area per molecule, $Å.^2$	Film thickness, Å.
0.15	..	..	..	..	End of monolayer	
.2	22.5	4.3	18.7	5.2	16.8	5.8
.4	21.6	4.5	17.3	5.7	14.3	7.0
.6	20.6	4.7	15.9	6.1	11.8	8.2
.8	19.6	5.0	14.5	6.7	7.6	12.8
.88	..	..	12.9	7.6	..	..
.90	19.1	5.1	Values calculated from the data of H. K. Livingston, Ph.D., thesis, University of Chicago, Dec., 1941.			
.95	16.6	5.9				
.99	11.2	8.7				

The lattice constants of these three types of crystalline solids indicate that the first monolayer of propyl alcohol should exhibit at a given vapor pressure, the most loose packing on barium sulfate, the tightest on quartz, with that for anatase intermediate.

The end of the monolayer on the surface of the solid occurs at a relative pressure (p/p_0) of about 0.9 (which is very high) with barium sulfate, at about 0.2 with anatase, and about 0.15 with quartz. With quartz the second layer is completed at a relative pressure of about 0.7. Since there is no known method of determining at just what pressure the second layer is actually completed, it is assumed that when the first monolayer is completed the propyl alcohol molecules are closely packed, and the same assumption is made for the second layer. Thus where the area per molecule adsorbed is equal to that which a propyl alcohol molecule should exhibit in perpendicular orientation, it is considered that the film is a monolayer, and if the mean molecular area is half as large, the film is assumed to be two molecules thick.

While the literature contains a very great number of isotherms which represent the adsorption of vapors upon the surfaces of solids, it is unfortunate that most of these isotherms were obtained with porous solids, where adsorption and capillary condensation are inextricably mixed. It is also unfortunate that a large percentage of the work on non-porous solids has not been carried to saturation of the vapor. Thus the literature gives almost no data which help in the development of a theory of adsorption uncontaminated by the effects of capillary condensation.

8. Theory of Adsorption.—This paper has considered the decrease in the surface enthalpy which occurs when a film of any thickness is adsorbed upon the surface of a solid. This decrease of enthalpy is equal, within the limits of experimental accuracy, to the decrease ($-\Delta E$) in surface energy. In the case investigated the angle of contact between the solid and liquid is zero. In such a case the amount of vapor adsorbed increases very rapidly with pressure at the lower values of p/p_0.

The relations are very different with a system such as that of water on graphite or on paraffin, which exhibit contact angles of 85.5° and 105 to 111°, respectively. There seem to be no carefully determined adsorption isotherms for a case of this type. A sample of graphite used with water in this Laboratory was found later to contain about 10% of ash, which may have greatly distorted the adsorption isotherm. With pure graphite the adsorption isotherm should be of Type III (convex to the pressure axis).

With films of this type the amount adsorbed increases with extreme slowness with pressure at low relative vapor pressures. The simplest explanation of non-spreading of the liquid in such a case would be to assume that even close to saturation the surface of the graphite (or paraffin) is sparsely populated by water molecules, and that there are many holes of molecular dimensions in the water layer. This gives so few points of attachment for the liquid water that the latter does not spread.

The theory of adsorption may be stated very simply as follows: Adsorption in any closed system which contains a solid and a vapor continues as long as the process can occur with a decrease of the Helmholtz free energy (A), while at constant pressure the condition is the same with respect to the Gibbs free energy (F). Since for unit area of the solid the decreases of free energy on adsorption is represented by

$$-\Delta F = -\Delta\gamma = \pi$$

the value of the film pressure (π) gives the decrease in free energy per unit area. It is not at all difficult to calculate π at any vapor pressure (p) if data are available for the adsorption isotherm at all pressures below p down to sufficiently low pressures. This is done by the method of Bangham.[12]

By a consideration of this free energy decrease on adsorption, and a simple assumption, a method has been developed for the determination of the area of a solid from an adsorption isotherm.

The free energy changes involved in adsorption will be treated in a later paper of this series. The free surface energy of *decrease* (π) of the surface of a solid increases with increase of thickness of a film upon it. Since $\pi = -\Delta\gamma$, the free surface energy decreases with thickness of the film.

From our calorimetric measurements the decrease of internal or "total" surface energy $(E_S - E_{S_f}) = (h_S - h_{S_f})$ may be calculated. The values of this quantity, together with the related values of the *decrease* of free surface energy, and of the latent heat $[T(s_S - s_{S_f})]$, where s is the entropy, are represented in Fig. 9.

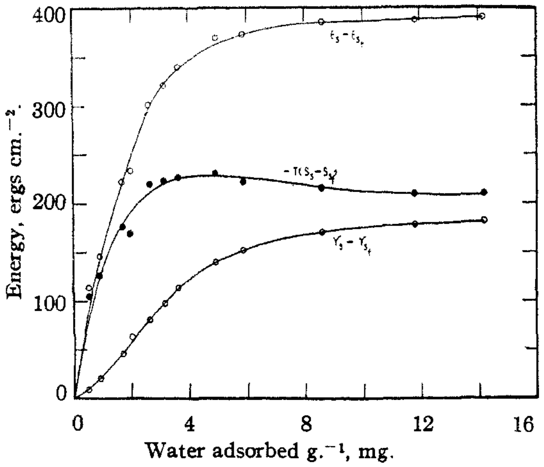

Fig. 9.—Lowering of the surface energy of TiO_2 (anatase) by an adsorbed water film. The *lowering* of the total surface energy is $\epsilon S - \epsilon S_f$, of the free energy $\pi = \gamma S - \gamma S_f$. and of the latent heat $l = T(sS - sS_f)$, where s is the entropy per unit area.

All of these quantities increase very rapidly at first with the amount adsorbed, but the free energy changes much less rapidly than either the total surface energy (E) or the latent heat ($l = TS$). It should be kept in mind that increases in the values of these quantities, which give the effects of the film on the surface of the solid, represent *decreases* in the surface energy of the solid. Thus the maximum in the curve for latent heat in Fig. 9 represents a *minimum* latent heat for the film covered surface of the solid. This minimum begins at approximately the end of the adsorption of the first monolayer, and the beginning of the deposition of the second layer.

9. Absence of an Effect of Closer Packing upon the Amount of Butane Sorbed at High Relative Vapor Pressures (Note: Added December 15, 1943).—In our work on the adsorption of butane and other vapors there had been no attempt to pack the powder tightly, so it was deemed advisable to determine whether a tighter packing would increase the amount of vapor taken up. If capillary condensation is an important factor in the process of sorption, then a significant increase should accompany the tighter packing.

An electron microscope photograph of the anatase used in this work was obtained at a magnification of 45,000 and this shows that it consists largely of aggregates. These give a very loose packing of the powder in the glass bulb where the sorption takes place. Thus with the ordinary type of packing in the bulb of 27 cu. cm. capacity, it was found in one experiment that only 3.78 cu. cm. of anatase was present, and this is approximately the average amount found. It is simpler to consider the volume of anatase per cu. cm. of capacity of the bulb. This amounts to 0.14 cu. cm. or 14%, so that the free space is 0.86 cu. cm. or 86%. Of this free space between 0.0429 and 0.0527 cu. cm. is filled up by "liquid" butane. Here 0.068 cu. cm. is the highest value attained at a pressure below that of saturation, and 0.078 cu. cm. is a value obtained at saturation. As usual the volumes given for the adsorbed film of butane do not represent its actual volume, but that of the same mass of liquid butane at −0.3° and 760 mm. pressure.

Later, additional anatase powder was packed in the bulb by tapping the bottom of the bulb on the wooden top of a desk until no tighter packing could be obtained by this means, when 4.61 cu. cm. of anatase was found to be present. The

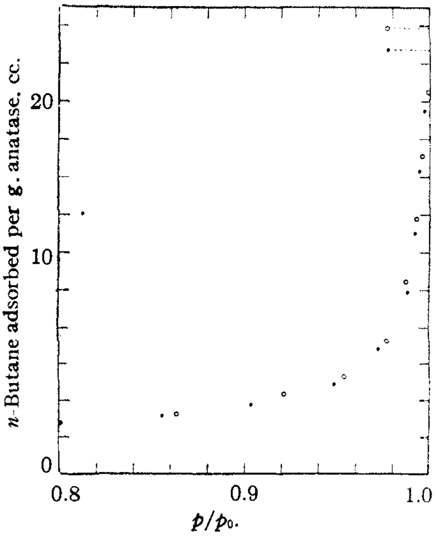

Fig. 10.—Effect of change of spacing between crystals and crystalline aggregates upon the amount of butane adsorbed at high relative pressures. Black circles indicate tighter packing, and open circles looser packing. Within the limits of experimental error the two curves are identical and no effect of packing is indicated. The dotted lines indicate the amount adsorbed at $p/p_0 = 1.0$.

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[12] D. H. Bangham, *Trans. Faraday Soc.*, **33**, 805 (1937): Bangham and Razouk, *ibid.*, **33**, 1463 (1937): *Proc. Roy. Soc.* (London), **A166**, 572 (1938).

new volume relations were per cm.^{3}: 0.171 cu. cm. of anatase in the vacuum, 0.829 cu. cm. of free space. The volumes of butane, calculated as liquid taken up just below and at saturation, were 0.0580 and 0.0673 cu. cm., respectively. These values are higher than for loose packing on account of the greater mass and area of the powder in the bulb.

The two adsorption isotherms for the looser and tighter packing, as given in Fig. 10, are the same within the limits of experimental error and give no evidence that the tighter packing increases the amount of butane sorbed. This might not be the case if the butane vapor in the bulb were kept extremely close to saturation for a very great length of time. In the determination of adsorption at lower pressures the time is extended until equilibrium is attained. For the highest pressures indicated there was no change of pressure (0.1 mm. can be detected with certainty) in four hours at $p/p_0 = 0.9990$ for the more tightly packed sample, and no change in fourteen hours at $p/p_0 = 0.9976$ for the more loosely packed sample. From this evidence it seems that capillary condensation cannot play any significant role.

While this paper deals principally with adsorption on a single solid, the writers have determined similar adsorption isotherms for more than one hundred solids, and have obtained equations for the isotherms which represent the behavior of condensed, intermediate, expanded, and gaseous films on solids. Two condensed phases have been discovered, so that we have now found five phases in films on solids. Some of these equations give remarkably accurate values of the area of the solids.

Summary

1. Almost all of the films adsorbed on the surfaces of non-porous solids, which have been investigated thus far, are highly polymolecular at vapor pressures very slightly below saturation.

2. For the first time, a determination has been made of the effect of distance on the intermolecular attraction (in energy units) between a solid and an adjacent liquid or adsorbed film. This energy of interaction is found to suffer a decay which is essentially an exponential function of the distance.

3. At 25°, the energy of vaporization of water is 10540 cal. mole^{-1}. If, however, the water is in the form of a monolayer on the otherwise clean surface of crystalline titanium dioxide (as anatase) the heat of vaporization is increased by 62%, or by 6550 cal. mole^{-1}. For the second layer this is reduced to a 13% increase, or 1380 cal. mole^{-1}, for the third to 4%, or 450 cal. mole^{-1}, while for the fourth and fifth layers, the values are of the order of 80 and 40 cal. mole^{-1}. These energy values indicate that the film of water adsorbed on titanium dioxide (anatase) should attain a minimum thickness of 5 molecular layers before saturation of the vapor is attained. Measurements of the thickness of the film just below saturation show that this is justified, since the thickness attained is over 15 Å. (five molecular layers). The measured thickness attained is 36 Å. or 10 molecular layers for nitrogen at −195.6°. Non-polar adsorbates attain considerable thicknesses. Thus *n*-butane at 0° attains a thickness of 64 Å., while the thickness of the first molecular layer is only about 4 Å., since the molecules *lie flat on the surface*. However, in the sixth or seventh layer, the degree of orientation should be small, and in the surface of the film should exhibit practically the same orientation as that in the surface of liquid butane at the same temperature. The thickness of this film is about 11 or 12 molecules.

4. The results obtained are contrary to Langmuir's theory of the general occurrence of monomolecular adsorption at vapor pressures moderately close to saturation. They also show that the combined monolayer plus capillary condensation theory, upheld by a large number of the workers in this field, is incorrect. They do not show that monomolecular adsorption cannot occur, nor are they in opposition to the idea that capillary condensation may occur in porous solids. They do show that *ad*sorbed films on plane surfaces commonly attain greater thicknesses than in porous solids. However, this should not be the case for water on hydrophobic solids, nor is it true for propyl alcohol on barium sulfate.

5. The theory of adsorption favored by these results is in agreement with the general picture indicated by the multimolecular theory of Brunauer, Emmett and Teller (BET). However, we show the incorrectness of one of the primary assumptions in their more simple theory: that the energy of vaporization of the second adsorbed layer is no greater than the energy of vaporization of the liquid, or $E_2 = E_L$. This is not offered as an adverse criticism of their theory, since this assumption was introduced by them in order to obtain a simple, two-constant adsorption isotherm. The areas given by their simple theory are surprisingly good, but the energy values ($E_1 - E_L$) are much too low. (The BET theory gives a value for $E_1 - E_L$ of 2100 cal. mole^{-1} while our experimental result corresponds to 6550 cal. mole^{-1}.) The great usefulness of their isotherm lies in the fact that it is the first and only method for the calculation of the number of molecules in a complete monolayer when the isotherm is of the sigmoid (S) or common type. The Langmuir equation also gives the number of molecules, but with non-porous solids there seems to be, unfortunately, only one known case to which it can be applied.

6. Evidence is presented which indicates that capillary condensation does not play any significant role in the sorption with a crystalline powder of the type used in this work.

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