[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Heats of Adsorption. V. Adsorption on a Homogeneous Surface[1]

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Ethyl chloride isotherms on a graphite of very uniform surface show lateral interaction effects that are usually obscured in most isotherms by effects of non-uniformity of the surface. The isotherm for the uniform surface is initially convex and it increases in steepness with coverage, because of the effects of lateral interactions with previously adsorbed molecules. This effect persists until near completion of the first layer. Isosteric heats of adsorption increase with coverage and show a maximum near completion of the first layer. As much as half the observed net heat of adsorption may be due to lateral interactions.

In both the Langmuir and the BET isotherm equations simplifying assumptions are made that (1) the surface is uniform and (2) the effect of lateral interactions with previously adsorbed molecules is negligible in comparison to the interactions of adsorbed molecules with bare surface.

In 1939, Orr[2] published isotherms for argon and other gases on KCl crystals which showed evidence that the second of these assumptions is wrong. The crystals had presumably nearly uniform surfaces and Orr found that the isotherms were convex to the pressure axis rather than concave, the customary type II shape. Isosteric heat curves computed from his isotherms showed a rise with surface coverage and a maximum near completion of the first layer. He interpreted these two effects as indication of lateral interactions of adsorbed molecules with one another. Previously, in a theoretical discussion, Fowler[3] had predicted just the behavior found by Orr.

Orr's isotherm has such an unusual shape that Brunauer[4] did not even list it among the five standard types. Since 1939, the isotherms for non-porous surface have been almost universally found to be type II, or concave to the pressure axis up to near completion of the first layer. Because of this there has been a tendency until recently to ignore the effects of lateral interactions and to accept the Langmuir–BET assumptions as essentially correct. In the past five years, however, other investigators have found heat coverage curves like those given by Orr and more attention has been paid to lateral interaction effects. Beebe, Biscoe, Smith and Wendell[5] obtained calorimetric heats of adsorption for nitrogen on Graphon that initially fall, then pass through a minimum and rise with increasing coverage up to near completion of the first layer. Joyner and Emmett[6] reported isosteric heats for the same system in excellent agreement with the calorimetric values. Hill, Emmett and Joyner[7] have given a theoretical discussion of heats and entropies of adsorption based on the experiments of Joyner and Emmett. Isotherms of benzene and cyclohexane on Graphon from this Laboratory[8] give computed isosteric heat curves much like those for nitrogen. Rhodin[9] obtained similar results for the heats of adsorption of nitrogen on single crystal faces of copper.

The results indicate that the Graphon and the copper crystal surfaces are more uniform than surfaces previously studied. The effects of lateral interactions appear to be masked in studies with non-uniform surfaces by changes in the activity of the surface itself with coverage. Recently we have determined isotherms for a sample whose surface appears to be still more uniform than the Graphon sample used in the studies cited above and whose surface area is large enough to permit accurate adsorption measurements at low relative pressures. Results with this sample, a new Graphon,[10] bring out the effects of lateral interactions even more strikingly than the previous samples. We find that lateral interactions affect the shape of the adsorption isotherm and cause the heat curve to rise with coverage until the first layer is completed. The magnitude of the lateral interaction effect is comparable with the magnitude of surface–adsorbate interactions.

Experimental

Graphon is a graphitized carbon black made by heating Spheron Grade 6 carbon black to near 3000° in an electric furnace. It was prepared by Cabot and an older preparation has been widely distributed for use in adsorption studies. The properties of this sample have been described by others.[5,6] In 1951, a new sample was prepared in the Cabot laboratories, some of which was sent to us and was used in the present study. The surface seems to be more uniform than that of the old Graphon and the purity higher. The old sample used here contained a small percentage of combined sulfur, which seems to be completely absent from the new. The surface area of the new is about the same as the old, 80–90 sq. m. per g.

Ethyl chloride isotherms were measured at 0 and 10° with equipment previously described.[11] The amount adsorbed was determined by removing and weighing the sample bulb after each addition of vapor. A 13-g. sample was used, thus giving a total area near 1000 square meters. Pressures were measured by a McLeod gage below 5 mm. and by a mercury manometer above this. The p_0 readings were 472 mm. at 0° and 700 mm. at 10°.

Isotherms were determined both for the new Graphon sample and for Spheron Grade 6 carbon black, the latter as a check on the apparatus since the properties of Grade 6 black are well known from other work.[5,6,12]

Before starting an isotherm, samples were pumped to a good vacuum with gentle flaming. This treatment serves to remove water and other loosely held vapors but not oxygen complexes and tightly bound hydrocarbons from the Spheron.

Discussion

The low pressure regions of the 0° isotherms are shown on two scales in Fig. 1. Spheron gives a normal type II isotherm but the Graphon isotherm is distinctly different, being like the isotherms reported by Orr for KCl crystals. Up to about 0.3

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(1) This is a report of work conducted under Contract N8onr54700 with the Office of Naval Research.

(2) W. J. C. Orr, *Proc. Roy. Soc.* (*London*), **A173**, 349 (1939).

(3) R. H. Fowler, *Proc. Camb. Phil. Soc.*, **32**, 144 (1936).

(4) S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, p. 150.

(5) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, THIS JOURNAL, **69**, 95 (1947).

(6) L. G. Joyner and P. H. Emmett, *ibid.*, **70**, 2353 (1948).

(7) T. L. Hill, P. H. Emmett and L. G. Joyner, *ibid.*, **73**, 5102 (1951).

(8) R. N. Smith, C. Pierce and H. Cordes, *ibid.*, **72**, 5595 (1950).

(9) T. N. Rhodin, Jr., *ibid.*, **72**, 5691 (1950).

(10) Furnished by Dr. Walter R. Smith of Godfrey L. Cabot, Inc., Boston, Mass.

(11) R. N. Smith, THIS JOURNAL, **74**, 3477 (1952).

(12) P. H. Emmett and R. B. Anderson, *ibid.*, **67**, 1492 (1945).

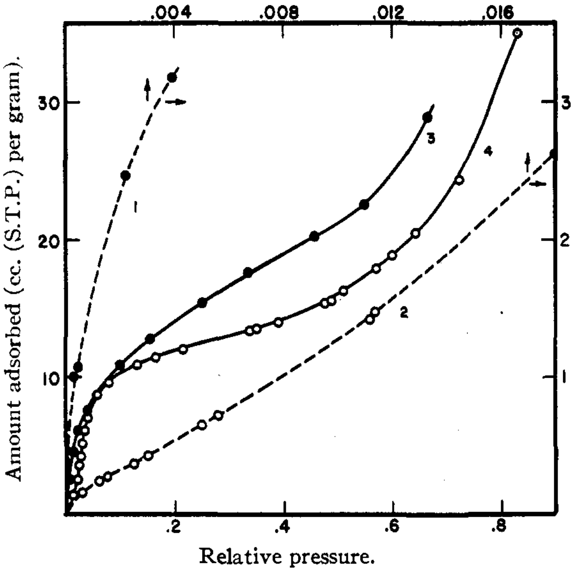

Fig. 1.—Ethyl chloride isotherms of Graphon and Spheron: O, Graphon; ●, Spheron. Dotted curves are for the very low pressure region. Refer to coördinates at right and top of sheet.

cc. of vapor per gram it is concave to the pressure axis. Then it changes to convex and the slope increases with further adsorption up to near completion of the first layer. Many more experimental points were obtained than can be shown in the plot, all falling on the smooth curve.

The Graphon isotherm indicates that the surface is unusually homogeneous. All sites, beyond the initial region up to 0.3 cc. per gram, appear to be of the same or nearly the same activity. As adsorption proceeds the molecules already on the surface increase the attraction for adsorbate, as postulated by Fowler. The Spheron surface is, as shown by others, non-uniform. As adsorption proceeds the nature of the surface changes with coverage and consequently the effects of lateral interactions do not show up in the isotherm.

Beyond the first layer the Graphon and Spheron isotherms have somewhat different shapes, showing that the second layers build up differently for uniform and non-uniform surfaces.[13]

Isosteric heats of adsorption were computed from the 0° and the 10° isotherms for Graphon. The heat curve is plotted in Fig. 2. Smoothed isotherms were used rather than individual points, to minimize small experimental errors that may cause very large errors in the computation, especially in low pressure region. The computed heats for low coverage are not thoroughly reliable, but it is significant that we find no region of the first layer in which the heat decreases with coverage, as has been found for heats of adsorption on the old Graphon sample.

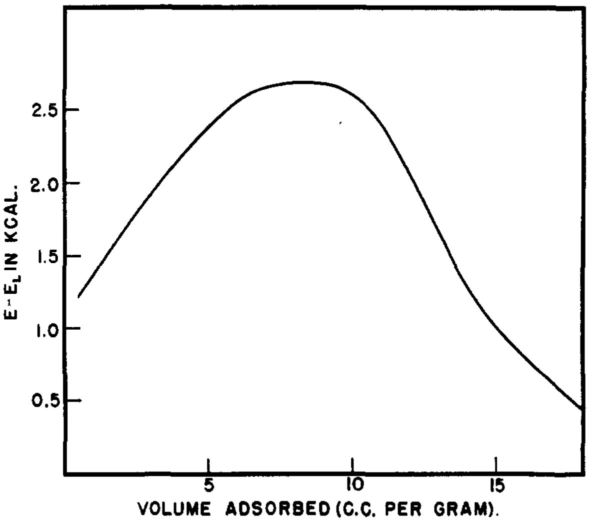

Fig. 2.—Isosteric heats of adsorption for ethyl chloride on Graphon. Data taken from smoothed isotherms at 0 and 10°.

The heat curve shows that the net heat of lateral interaction may be as large as the net heat of surface–adsorbate interaction. At the lowest coverage for which the heat could be computed $E - E_L$ is 1.0–1.5 kcal. per mole. Near completion of the first layer the value rises to near 2.5 kcal.

Heat curves for Spheron[5,6] start at a high value and drop with coverage, leveling off somewhat near V_m. Here the lateral interaction effect, although still present, is masked by the decrease in the surface–adsorbate heat and the net result of a drop in one and a rise in the other is to make the curve level off.

Spheron has so much adsorption at low relative pressure that isosteric heats could not be accurately computed from its isotherms for the first half monolayer adsorbed. That is, the pressures were so low that the ratios in pressures for a given adsorption at 0 and 10° could not be determined with sufficient accuracy to permit use of the Clapeyron equation. The isotherms indicate that Spheron must have a much higher initial heat of adsorption than Graphon, which is in line with other work.

The distinctive isotherm of the new Graphon, together with the accumulated heat of adsorption data, indicate that much of the existing data for adsorption on non-porous surfaces are based on non-uniform surfaces. In reality, the typical isotherm of a plane surface may be, as predicted by Fowler, the convex type we find in Fig. 1. The existence of a concave type II isotherm may *per se* indicate a non-uniform surface. It is of considerable theoretical interest to find whether the low pressure adsorption of nitrogen or argon on new Graphon will give a convex or concave isotherm.

The nature of the heterogeneity of surfaces, which causes the isotherm to be type II, is not known. Orr believed it to be small fissures in which molecules are held by two walls. Other explanations are that the surface has steps at which the

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(13) Private communications from Prof. R. A. Beebe and Dr. W. R. Smith state that they have independently found the low temperature isotherms for new Graphon to show steps corresponding to adsorption in the second and third layers. This indicates that on the very uniform surface there is a tendency for each layer to be essentially completed before another starts to form. The ethyl chloride isotherm does not show this effect. We think the difference might be due to the higher temperature used for the ethyl chloride adsorption. The thermal agitation might tend to wash out weak surface forces extending beyond the first layer. Neither Beebe nor Smith reported finding a convex isotherm for first layer adsorption, such as the ethyl chloride shows.

adsorbed molecule can be held jointly by two walls or that there are impurities in the surface that increase the attraction of some sites for adsorbate. As noted above, the new Graphon has a small portion of super-active surface amounting to some 3% of the total. The old Graphon apparently had about 50% of the surface more active than the average, since the heat curves dropped until the surface was about half covered.

When a surface is heterogeneous the writers feel that the computation of spreading pressures from isotherms may be misleading. Adsorption will tend to be localized on a non-uniform surface, the first molecules migrating to the sites of highest activity and remaining there. Only when all surface sites are of equal activity will an adsorbed film behave as a true two dimensional gas and spread uniformly.

ADDED IN PROOF.—A recent paper by Halsey,[14] not available when this manuscript was submitted, contains several points of interest in relation to the present results. We agree with Halsey's conclusions regarding the importance of coöperative forces in adsorption but feel that his equations do not adequately describe real isotherms. In Fig. 2 of his paper Halsey shows the calculated isotherm for a uniform surface to rise more steeply than the one for a surface of "great heterogeneity." Our experimental results show just the opposite effect; the Spheron isotherm is much steeper initially than the Graphon isotherm. Halsey assumes that the isotherm for a very inhomogeneous surface may have a pseudo "point B" far below completion of the first layer. This again is contrary to what we find for Spheron and to the majority of isotherms in the literature. In his calculated isotherm for the uniform surface, where coöperative adsorption is important, Halsey gives a curve concave to the pressure axis below point B, contrary to the actual behavior of the Graphon isotherm. We find no indication in the ethyl chloride isotherm of stepwise adsorption as postulated by Halsey, but as noted above[13] isotherms of others at liquid nitrogen temperature have shown such a behavior.

Another reference not previously noted is the work of Jura and Criddle,[15] who find the isotherm of argon on a graphite sample to have the convex shape below point B that we find for the Graphon isotherm. This provides still additional indication that the true isotherm for a uniform surface must have this shape.

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[14] G. D. Halsey, "The Role of Surface Heterogeneity in Adsorption," Volume IV, Advances in Catalysis, Academic Press, Inc., New York, N. Y., 1952.

[15] G. Jura and D. Criddle, *J. Phys. Colloid Chem.*, **55**, 163 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

Purple Sulfur, A New Allotropic Form[1]

BY FRANCIS OWEN RICE AND CALVIN SPARROW

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According to vapor pressure measurements, sulfur vapor in the pressure range 0.1–1.0 mm. and the temperature range 500–700° consists almost entirely of S_2 molecules. We have found that these may be frozen out on a liquid nitrogen cooled surface to give a purple solid. On warming to room temperature, this changes in the course of a few seconds, to a mixture containing about 40% of crystalline sulfur and 60% of amorphous sulfur. The activation energy of the change is 3.1 kcal.

A very large number of allotropic forms of sulfur has been reported and detailed confirmation of the existence of at least three forms has been published. At ordinary temperatures the stable solid form consists of an S_8 ring.[2] At temperatures above about 160°, liquid sulfur consists largely of long chains which on sudden cooling to room temperature form the unstable amorphous sulfur, $S\mu$. In the temperature range 500–700° and the pressure range 0.1 to 1.0 mm., the vapor consists essentially of S_2 molecules formed by dissociation of S_8 in accordance with the equilibrium,[3] $S_8 \rightleftarrows 4\ S_2$. Both solid and liquid sulfur are diamagnetic but the vapor is paramagnetic[4] and measurements on the susceptibility of sulfur vapor indicate that S_2 has the theoretical moment of the triplet state. There is some uncertainty as to the method of dissociation of sulfur in the vapor state and intermediates such as S_4 and S_6 have been postulated in order to reconcile vapor pressure and vapor density measurements. In the following series of equilibria

$$S_8 \rightleftarrows 4S_2 \qquad S_6 \rightleftarrows 3S_2$$
$$S_4 \rightleftarrows 2S_2 \qquad S_2 \rightleftarrows 2S$$

it seems to be fairly well established that at 450° the vapor consists of over 99% S_2 at 0.1 mm. pressure, and 55% S_2 at 1 mm. pressure. At 500°, the vapor consists of almost 100% S_2 at either 0.1 mm. or 1.0 mm. pressure. The dissociation of S_2 into monatomic sulfur begins to be appreciable only at very high temperatures (1200°) even at 0.1 mm. pressure.

The present investigation was undertaken with the object of studying these equilibria by attempting to isolate one of the high temperature forms, S_2, using a technique described in a previous article[5] in which an equilibrium or stationary state was established at high temperatures in a flowing system at low pressures and the gases were suddenly cooled

[1] Taken from the dissertation presented by Calvin Sparrow for the Degree of Doctor of Philosophy in The Catholic University of America.

[2] B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

[3] G. Preuner and W. Schupp, *Z. physik. Chem.*, **68**, 129, (1909); W. Klemm and H. Kilian, *ibid.*, **B49**, 279 (1941); H. Braune, S. Peter and V. Neveling, *Z. Naturforsch.*, **6a**, 32 (1951).

[4] L. Néel, *Compt. rend.*, **194**, 2035 (1932); A. B. Scott, THIS JOURNAL, **71**, 3145 (1949).

[5] F. O. Rice and M. Freamo, *ibid.*, **73**, 5529 (1951).