

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Phase Transitions in Surface Films on Solids¹

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Published isotherms of *n*-heptane on Fe₂O₃ and graphite have been redetermined using a gravimetric method and McLeod gage instead of a volumetric method and cathetometer. The present results are at variance with the others in that no first- or second-order phase transitions are observed.

In 1937 Bangham² showed that the Gibbs adsorption equation could be applied to the adsorption of vapors at solid surfaces and that the reduction in free surface energy can be identified with a tangential spreading pressure of a surface film. Such a spreading pressure of an adsorbed film on a solid surface cannot be measured directly, as it can for a film on a liquid surface, but it can be calculated by use of the equation (with symbols employed by various authors)

$$\varphi = \pi = \sigma_s - \sigma = \gamma_s - \gamma_{sl} = RT \int_0^P \Gamma \frac{dP}{P}$$

where φ , etc., is the spreading pressure and Γ is the surface concentration in excess of that in the gas phase. Using these computed spreading pressures Gregg,³ Harkins and associates⁴⁻⁹ and others¹⁰⁻¹² have interpreted films on solids by drawing analogies to the known properties of insoluble films on liquids.

The strongest direct evidence in support of the view that films on solid surfaces behave like insoluble films on liquids is the existence of discontinuities in experimental adsorption isotherms when the fraction of the surface covered is less than unity. Benton and White,¹³ Ross and Boyd,¹⁴ and Harkins, Jura and Loeser,⁵⁻⁹ have reported isotherms showing such discontinuities. In most cases the samples were of a type that one would not expect to possess uniform surfaces and consequently the occurrence of first order phase transitions is difficult to explain.

On re-examination of this work it is noted that for most of the *n*-heptane cases cited by Harkins, Jura and Loeser the phase transitions occur at about the same absolute pressure, regardless of the adsorbent used or the temperature. It is also noted that the isotherms for different temperatures cross one another in such a manner as to indicate both

positive and negative net heats of adsorption over a narrow temperature range. This behavior is contrary to general experience, as the authors point out. Further, the molecular areas calculated for the adsorbate held in these monolayers are enormously large, thus indicating a phase transition where but a fraction of the surface is covered.

For these reasons and because of the importance of these phase transitions in theoretical interpretations of adsorption and of the nature of surface films, it was decided to repeat some of the isotherms of others by a different method. The two systems which we felt had been investigated in greatest detail, *n*-heptane on ferric oxide and *n*-heptane on graphite, have been studied again with great care at various temperatures. No evidence of a phase transition was found for either system.

Experimental

The *n*-heptane used for these measurements was purchased from the National Bureau of Standards with the impurity given as 0.1 mole per cent. It was stored over outgassed metallic sodium for several months before distillation *in vacuo* to its reservoir in the vacuum line. The Fe₂O₃ was Baker and Adamson, reagent grade, with the maximum limits of impurities listed as 0.25% insoluble in HCl, 0.25% SO₄, 0.005% Cu, 0.005% Zn and 0.20% substances not precipitated by NH₄OH. The graphite sample was obtained from the laboratory of W. D. Harkins and was thought to be like the sample for which Harkins, Jura and Loeser report their phase transitions.

The degassing procedure of Harkins, Jura and Loeser⁶ was at first followed, namely, evacuation at room temperature for several hours followed by heating *in vacuo* for 14 hours at 525° and subsequent cooling *in vacuo*. The samples were open to continuous pumping during all stages. It was found that this procedure did not satisfactorily outgas the samples, for the pressure build-up in our vacuum system was about 5 × 10⁻⁵ mm. per hour for Fe₂O₃ and about 15 × 10⁻⁵ mm. per hour for the graphite over a two-day period compared to a pressure build-up of 1.6 × 10⁻⁵ mm. per hour for the same system without the samples. The adsorbent samples as finally used were exposed several times to *n*-heptane vapor and outgassed *in vacuo* overnight at about 500° between exposures. The total heated degassing time for each sample was well over 50 hours. At the completion of each isotherm, the adsorbent was outgassed overnight at 200° and its weight checked to ascertain whether permanent weight changes had occurred during the course of a series of measurements. These weights always checked to within 0.3 mg. of the original weight, an amount which corresponds to 2.9 × 10⁻³ cc. (S.T.P.) per gram for Fe₂O₃ and 2.0 × 10⁻³ cc. for graphite. The graphite sample weighed 33.5 g. and the Fe₂O₃ weighed 23.1 g. The Fe₂O₃ was not really outgassed by this procedure, for by putting a sample of Fe₂O₃ into a quartz vessel and heating it to successively higher temperatures, successively greater weight losses were observed accompanied by sintering and a great reduction in bulk volume. An isotherm run on the sintered sample showed considerably less adsorption than for the sample given the usual treatment. The treatment described does, however, give a satisfactory low pressure and the weight remains constant.

The vacuum system included a medium-pressure McLeod gage, two reservoirs for *n*-heptane, precision-ground hollow

(1) This is a progress report of work done under Contract N8-ONR-54700 with the Office of Naval Research.

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

(3) S. J. Gregg, *J. Chem. Soc.*, 696 (1942).

(4) G. Jura and W. D. Harkins, *THIS JOURNAL*, **66**, 1356 (1944).

(5) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **13**, 535 (1945).

(6) W. D. Harkins, G. Jura and E. H. Loeser, *THIS JOURNAL*, **66**, 554 (1946).

(7) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **14**, 117 (1946).

(8) G. Jura, W. D. Harkins and E. H. Loeser, *ibid.*, **14**, 344 (1946).

(9) J. Alexander, "Colloid Chemistry," Vol. VI, Reinhold Publishing Corp., New York, N. Y., 1946, chapter 1 by W. D. Harkins and G. Jura.

(10) W. G. Palmer, *Proc. Roy. Soc. (London)*, **A160**, 254 (1941).

(11) M. H. A. Armbruster and J. B. Austin, *THIS JOURNAL*, **66**, 159 (1944).

(12) M. A. Cook and D. H. Pack, *ibid.*, **71**, 791 (1949).

(13) A. F. Benton and T. A. White, *ibid.*, **53**, 3301 (1931).

(14) S. Ross and G. E. Boyd, Document MDDC-864, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. Declassified April 11, 1947.

plug stopcocks, and mercury cut-offs at each stopcock (with exception below) to minimize the possibility of evolution of *n*-heptane from stopcock grease. Pumping was aided with a two stage mercury vapor diffusion pump. High vacuum silicone grease was used and tested for satisfaction. The sample bulb stopcock, the T-S joint of the bulb to the vacuum system and the stopcock on the system at this connection could not be eliminated by a mercury cut-off.

The McLeod gage was such that for the lowest pressures measured, an observed pressure difference of 0.1 mm. corresponded to an actual pressure difference of 1.31×10^{-4} mm. The observed pressure differences were read to the nearest 0.1 mm. with the aid of a thermometer reading lens fashioned to give reproducible positioning against the manometer tubes of the McLeod gage. The observed pressure differences did not usually exceed 20 mm., and in the region of expected phase transitions it never exceeded 15 mm. To test the deviation to be expected from the ideality of *n*-heptane under various pressures in the McLeod, a given sample of *n*-heptane was measured at actual pressures in the McLeod ranging from 0.1 to 15 mm. The variations observed in the *PV* products were all within the limit of the ability to read the observed pressure to 0.1 mm. It was thus concluded that under the conditions of use, the McLeod gage was satisfactory for all pressure measurements. An observed pressure was recorded only after ascertaining by successive measurements that constant pressure had been reached. No point was taken in less than two hours after addition of *n*-heptane; many were given a very much longer time. For all isotherms data were obtained up to relative pressures of 0.33.

For measurements below room temperature, the *n*-heptane was stored in the reservoir in the constant temperature bath; for those above room temperature, it was stored in a bulb cooled by ice. For all measurements below room temperature, P_0 was observed by direct measurement of the vapor pressure of *n*-heptane. For all runs, the constant temperature bath temperatures were measured with a thermometer calibrated by the National Bureau of Standards. In cases where direct comparison of thermometer and vapor pressure data were possible, excellent agreement was obtained. Values of P_0 above room temperature were determined from published vapor pressure data¹⁶⁻¹⁷ and the observed temperatures. For the experimental temperatures of 8.1, 14.6, 21.1, 27.6, 34.3 and 41.0°, the P_0 values are 18.5, 26.6, 37.3, 52.2, 71.0 and 97.5 mm., respectively. Below room temperature, temperature control was obtained in a vigorously stirred 9-gallon bath by means of a specially designed refrigeration unit which ran continuously in opposition to an intermittent electric heater activated by a Merc-to-Merc thermoregulator and relay. Cool tap water replaced the refrigerator unit above room temperature. Bath temperature was controlled to within $\pm 0.02^\circ$.

The amount of adsorption occurring at each pressure was determined gravimetrically. When equilibrium had been reached, the sample bulb was detached from the system, the silicone grease removed from the taper joint connection, and the bulb wiped with a damp, lintless cloth. It was then weighed to the nearest 0.1 mg. against a tare bulb of approximately the same surface area. Long waiting periods on the balance were used to insure correct weight. Before starting the measurements, the stopcocks on the sample bulbs were worked long and vigorously and all excess grease removed with great care to avoid possible weight loss later during a series of adsorption measurements. These stopcocks were not submerged below the surface of the water in the constant temperature-bath. Special precautions were taken for the measurements below room temperature in ensuring against the distillation of mercury into the sample bulb during periods in which the system was being pumped out preparatory to addition of more *n*-heptane to the sample bulb. Earlier experiments had demonstrated that this could occur easily at room temperature under small temperature gradients. The reproducibility of the original weight of the outgassed sample on completion of an isotherm testifies to the care of these measurements. At each pressure, where significant, correction was made for unadsorbed

vapor in the sample bulb. This correction was negligible below 0.7 mm. for Fe_2O_3 and below 0.4 mm. for graphite.

Results

Our results are summarized in Figs. 1-4 along with representative Harkins, Jura and Loeser curves for comparison. We have also plotted our data using relative pressure instead of absolute pressure, and find that in each case more adsorption occurs at a lower temperature for a given relative pressure. We have not shown these plots because the curves are so close together.

Not only did we observe no first-order phase transitions but neither did we observe second-order phase transitions in the case of *n*-heptane on graphite. For both adsorbents we found greater adsorption than Harkins, Jura and Loeser at the very low pressures, but as nearly as can be judged from the published isotherms, the amount of adsorption is just the same as theirs at higher pressures. In other words, our point B would be the same as theirs.

We have tried unsuccessfully to find the reasons for the difference between our results and those of Harkins, Jura and Loeser. It may be that our samples are not the same as those used by them (we did use the same brand and grade). The temperatures of our baths seem to be regulated with the same tolerance, and the *n*-heptane seems to be of the same high quality.

Our techniques do differ in three major ways. As previously described, the outgassing procedure used by them was not adequate for us. Instead of the volumetric method, we used a gravimetric method which is free of the potential danger of accumulating foreign or displaced gases. This may be very important at very low pressures, especially if there is a tendency for the sample to build up pressure of its own accord. In the gravimetric method the whole system except the sample bulb itself is highly evacuated between each isotherm point; this would tend to minimize such an effect. Finally, whereas we used a McLeod gage for pressure measurements, they used a manometer "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 0.01 mm., and its errors are known to 0.001 mm."⁴ In our measurements, the observation of a 0.1 mm. pressure difference corresponded to 1.31×10^{-4} mm., or better than a tenfold increase in sensitivity over their method. In this connection it may be noted that Whytlaw-Gray and Teich,¹⁸ after making a detailed study of the mercury meniscus and its bearing on the precision measurements of gas pressures, conclude that "a precision of ± 0.01 mm. in the pressure reading is about the limit of accuracy that can be reached with a good cathetometer and scale." Their discussion leads one to the conclusion that a cathetometer is not a suitable instrument for measurement of pressures as low as done

(15) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(16) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 224.

(17) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1939, p. 40.

(18) R. Whytlaw-Gray and N. Teich, *Trans. Faraday Soc.*, **44**, 774 (1948).

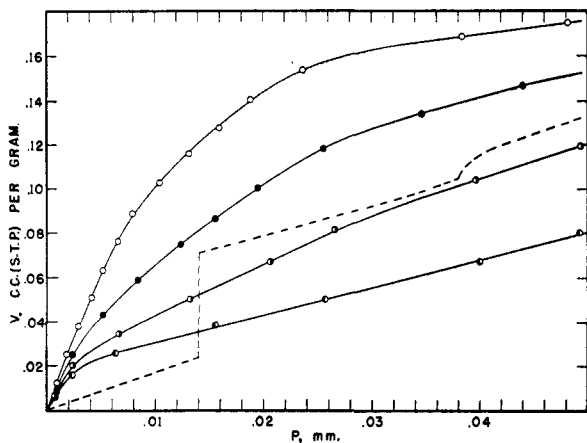


Fig. 1.—Low pressure adsorption isotherms of *n*-heptane on graphite: ○, 21.1°; ●, 27.6°; ◐, 34.3°; ◑, 41.0°. Dotted line is 25.0° isotherm of Harkins, Jura and Loeser on similar sample.

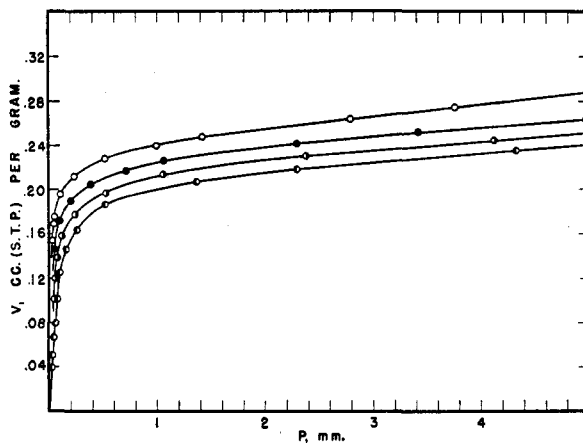


Fig. 3.—Medium pressure adsorption isotherms of *n*-heptane on graphite: ○, 21.1°; ●, 27.6°; ◐, 34.3°; ◑, 41.0°.

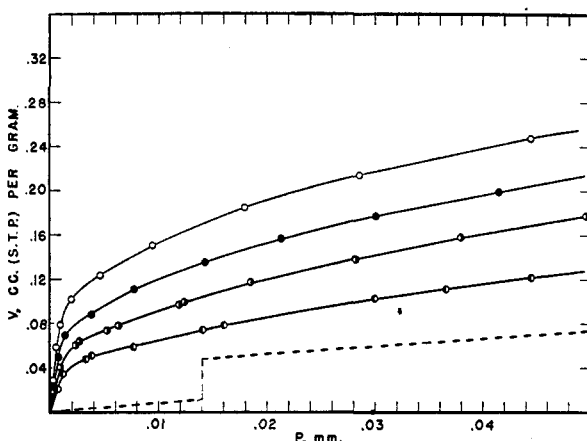


Fig. 2.—Low pressure adsorption isotherms of *n*-heptane on Fe_2O_3 : ○, 8.1°; ●, 14.6°; ◐, 21.1°; ◑, 27.6°. Dotted line is 22.0° isotherm of Harkins, Jura and Loeser for a similar sample.

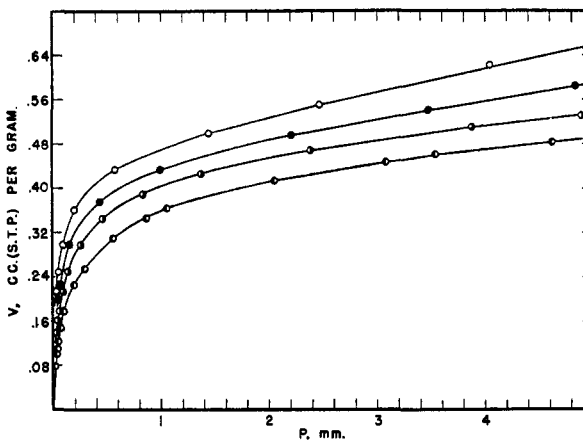


Fig. 4.—Medium pressure adsorption isotherms of *n*-heptane on Fe_2O_3 : ○, 8.1°; ●, 14.6°; ◐, 21.1°; ◑, 27.6°.

for these adsorptions. None of these factors, however, gives a satisfactory explanation for the observed difference.

Discussion

The lack of any discontinuity in our *n*-heptane isotherms for ferric oxide and graphite establishes a reasonable doubt as to the reality of phase transitions on heterogeneous surfaces when the fraction of the surface covered is small. We believe that the present status of these phase phenomena can be improved only by further investigation by others for various systems, using a variety of improved pressure and adsorption techniques.

A logical general concept of adsorption on heterogeneous surfaces might consider the surface film to be composed of two phases—two-dimensional liquid islands connected by a two-dimensional gas. The liquid islands exist on the more active adsorption sites of the solid, and as the pressure increases the

liquid phase increases as less active sites become effective. Thus, up to the formation of a monolayer there has been a continuous phase transition, but unlike the common transition phenomena it has occurred over a range of pressures. In special instances, solid surfaces may exist which do not have a continuous range of active sites, as in the case of the specially prepared crystals of sodium and potassium chloride used by Ross and Boyd¹⁴ for the adsorption of ethane at -183° . For such a surface, one might observe a discontinuity in the adsorption isotherm, not because of the occurrence of a special phase of the surface film, but because the existence of a large area of relatively uniform surface activity permits the normal process of adsorption to occur at a given pressure instead of over a range of pressures. Further, if a large number of discontinuities should exist in the same experimental isotherm, it would seem more logical to attribute the cause to surface heterogeneity of this type rather than to a large variety of surface film phases.

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