tration of vibrational levels in this region. Collision theory calculations show that mechanism A cannot explain values of recombination constants much higher than the values for the rare gases, even if a transfer of energy (reaction 4) occurred at every collision. The only significant contribution an energy transfer step involving degrees of freedom other than translational could make would be in connection with reaction 6; *i.e.*, the energy transfer theory can only be of importance if the complex mechanism C is in operation.

It cannot be claimed that the exact mechanism of recombination is known for any one system. The most plausible conclusion is that mechanisms B and C only are important and that the contribution of mechanism C probably increases with k_M. A possible explanation for the importance of mechanism B compared with mechanism A even for the rare gases may be that the field of M is more effective in the former case in weakening the selection rules which account for the theoretical statistical factor of $^1/_{16}$. The similarities between iodine and bromine atom recombination emphasize the fact that it is the intermolecular force field of the third body which is the main factor in determining the recombination rate constant, and that specific chemical interaction between atom and third body molecule is not involved.

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Physical Adsorption in the Multilayer Region on Heterogeneous and Homogeneous Surfaces

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Adsorption isotherms for a very uniform surface graphite, Sterling MT (3100°) are compared with those for less uniform surfaces. The isotherm of ethyl chloride on MT at −78° gives a well defined second layer step, as predicted by the Frenkel–Halsey–Hill equation, $-\ln p/p_0 = k/\theta^s$, but nitrogen at −195°, ethyl chloride at 0°, benzene at 20° and *n*-hexane at 20° do not show this step. Reasons are discussed for the differences. When there is normal free surface adsorption a log–log plot of amount adsorbed *vs.* log p_0/p is linear throughout the multilayer region for all isotherms except those with steps. Applications of such plots are made for several types of isotherms and interpretations are given. It is shown that customary BET nitrogen areas for uniform surface graphites are in error, being about 80% of the true value. The reason is loose packing of N_2 molecules at the inflection point marking the start of multilayer adsorption. The isotherm becomes normal above a relative pressure of 0.4.

Physical adsorption in the region up to completion of the first layer and slightly beyond is well described by the BET equation[1] when the surface is heterogeneous. This equation also fits isotherms on uniform surfaces when the lateral interaction forces are small, but when they are large and the surface is highly uniform the isotherm is convex to the pressure axis up to near completion of the first layer (as shown in the ethyl chloride isotherm of Fig. 2) and the BET equation does not apply until past the convex region. Isotherms of this shape may be described by an equation developed by Kiselev and associates,[2] which takes the lateral interaction forces into account.

Neither the BET nor the Kiselev equation will fit experimental isotherms far into the multilayer region. As shown previously[3] this region is well described for many isotherms by the equation

$$-\ln p/p_0 = k/\theta^s \qquad (1)$$

where k is a constant related to the energy of adsorption in the first layer, θ is the number of statistical layers and the exponent s is related to the fall-off of the van der Waals forces of the surface with successive layers in the adsorbed film. This multilayer equation was developed independently by Frenkel,[4] Halsey[5] and Hill.[6] It has the advantage of giving a linear isotherm when the amount adsorbed is plotted *vs.* log p_0/p on a log–log scale. Deviations from a linear plot are useful for detection of capillary condensation.[3] These results have led to further study of the FHH equation for multilayer adsorption on both heterogeneous and homogeneous surfaces.

Experimental

Isotherms have been determined for nitrogen at −195° and ethyl chloride at 0 and −78° for two types of surfaces, an anatase from the lot used by Jura and Harkins[7] and a graphitized carbon black from Cabot[8] designated Sterling MT (3100°). The anatase has a heterogeneous surface and the graphite one of the most homogeneous surfaces yet described.

The adsorption line, shown in Fig. 1, is designed to cover a wide range of pressures, for vapors whose p_0 varies from 2 mm. to one atm. It is conventional in principle but embodies several features which are found to facilitate ease and accuracy of operation.

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[1] S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

[2] A. A. Isirikyan and A. V. Kiselev, *J. Phys. Chem.*, **65**, 601 (1961); **66**, 205, 210 (1962). References are given to more extended treatment in the original Russian publications.

[3] C. Pierce, *J. Phys. Chem.*, **64**, 1184 (1960); **63**, 1076 (1959).

[4] J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, New York, N. Y., 1946.

[5] G. D. Halsey, Jr., *J. Chem. Phys.*, **16**, 93 (1948); *J. Am. Chem. Soc.*, **73**, 2693 (1951); **74**, 1082 (1952). See also *Can. J. Chem.*, **33**, 184 (1955); *J. Phys. Chem.*, **57**, 646 (1953); **58**, 1011 (1954); **61**, 1158 (1957).

[6] T. L. Hill, "Advances in Catalysis," Academic Press, New York, N. Y., 1952; *J. Chem. Phys.*, **14**, 264, 441 (1946); **15**, 767 (1947); **17**, 580, 668 (1949).

[7] G. Jura and W. D. Harkins, *J. Am. Chem. Soc.*, **66**, 1146 (1941).

[8] Provided by Prof. J. M. Holmes, Carleton University, Ottawa, Canada. See J. M. Holmes and R. A. Beebe, *J. Phys. Chem.*, **61**, 1684 (1957). Our sample appears to be from the lot used by Isirikyan and Kiselev, which they designate MT-1. Below $0.4p_0$ our data coincide with their isotherm. Above this pressure we obtain slightly higher adsorption than they, but in this region they show no data for MT-1. The deviation is probably due to experimental uncertainty in dead space measurement, as discussed later. Further investigation will be made of this.

Adsorbate is confined in the space to the right of manometer M_1 and all PV measurements are made at constant volume by adjusting M_1 to the zero mark. This adjustment is made by admitting air to the left-hand side through capillary leak L. Final adjustment is made by use of a mercury leveling bulb LB_1, attached to a mercury filled tube A. After this adjustment pressures above 20 mm. are read on manometer M_2. Smaller pressures are read on the McLeod gauge, Mc. The volume of the manifold system is varied as needed by use of calibrated bulbs B_1, B_2, and B_3 whose volumes are, respectively, 30, 100, and 500 ml. The volume of Mc is 150 ml. With no bulbs in use the manifold is 27 ml., the smallest volume used in any measurement. Bulb B_2 was calibrated by mercury before sealing to the line. It is used for calibrating all other volumes in the system.

Nitrogen is stored in reservoir R_2 which is fitted with a mercury leveling bulb, LB_2. Ethyl chloride is stored as liquid in R_1, kept at 0 or −78°, as convenient for the system in use.

For each point of an isotherm the desired quantity of gas is admitted into the manifold system, M_1 is adjusted to the zero mark, and the pressure measured. The left-hand side then is evacuated and gas admitted to sample bulb S. If above 20 mm. the equilibrium pressure is read on M_1 since constant volume is not required for this measurement. Small pressures are read by Mc, after first closing the stopcock for S. After equilibrium is attained S is closed, M_1 adjusted to zero by readmitting air at L, and the final pressure is read by M_2 or Mc.

The McLeod gage is designed for the pressure range 10^{-4} to 20 mm. The compression arm is evacuated, as shown in Fig. 1, to eliminate need for knowing the gas pressure above the mercury. (At high pressures the compression of the gas in the manifold as the mercury level rises makes necessary a variable correction of the residual pressure.)

The porous Pyrex discs,[9] shown as F_1 and F_2, are to prevent accidental surges of mercury into the line. Early attempts to operate the system without these discs led to considerable difficulty. A similar disc in the sample tube, F_3, effectively prevents any dusting of the powder particles into the line.

The dead space in S is measured in the conventional manner by helium, taking care that the bath level is at its normal operating position. The effect of slight variations in bath level is minimized by use of a capillary lead to S. In filling the tube care is taken to keep the dead space as small as possible. The tube is inverted and the powdered sample packed tightly onto the disc. The tube is then sealed off as closely as possible without overheating the sample. With a 4-g. sample of MT the dead space is 4.72 ml. but even this small volume makes for an appreciable correction at liquid nitrogen temperature, since the effective volume is then about 18 ml. With nitrogen at a relative pressure of 0.8 the unadsorbed vapor in S amounts to nearly 40% of the total admitted, and any error in computing the correction may cause an appreciable uncertainty in the isotherm at high relative pressures. In work with ethyl chloride at −78° the dead space correction for the same sample is very small, since P_0 is only 3.63 mm.

The saturation pressure, p_0, is measured along with each isotherm point by use of vapor pressure thermometers. The bulb used for ethyl chloride is shown at T in Fig. 1. The nitrogen thermometer is portable, not attached to the line. It is filled with pure gas at about 1000 mm. pressure.

Initially some difficulty was encountered in maintaining constant temperature with Dry Ice. This was eliminated by constructing a rubber hood over the Dewar flask which contains the Dry Ice. This hood is a sheet of thin rubber (dental dam) tied to the lead tubes and on the outside of the Dewar flask tightly enough to maintain a small positive pressure so that there is an atmosphere of CO_2 above the solid Dry Ice and water vapor is excluded. The Dry Ice is powdered and passed through a 10-mesh screen before packing into the Dewar. No solvent is used. After an initial period of adjustment, the temperature becomes very constant and during an isotherm determination p_0 seldom is found to vary more than 0.03 mm. from the normal value of 3.63 mm. It is found however that use of flasks of different sizes will give a somewhat different p_0 for ethyl chloride. The rubber hood also was found to be useful for liquid nitrogen baths. Temperature drift is minimized and condensation of oxygen and water vapor is eliminated completely.

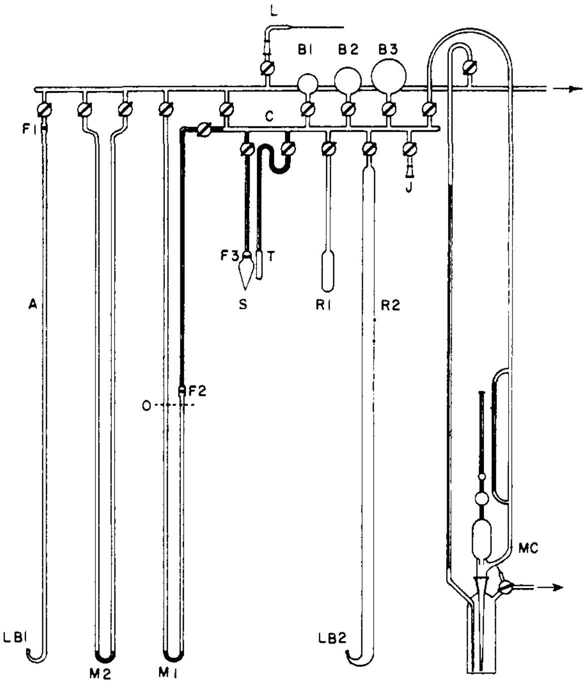

Fig. 1.—Adsorption line: the leveling bulbs, designated LB1 and LB2, are not shown. They are attached at the indicated positions by flexible hose.

At the conclusion of each isotherm the data are tested by warming the sample to room temperature and measuring the total vapor present. This is done volumetrically for nitrogen but ethyl chloride is conveniently adsorbed at −78° into a charcoal tube and weighed. In the isotherms at −78° the weight of vapor recovered usually agrees with the computed amount for the total separate additions within 0.1 mg. When volumetric isotherms were attempted with ethyl chloride at 0° (where p_0 is 471 mm.) there was not good agreement between the cumulative amounts added and the final recovery. It appears that at high pressure there is appreciable solubility of the vapor in stopcock grease, a solubility that will vary with the pressure. Because of this all ethyl chloride isotherms at 0° are made gravimetrically, by removing the bulb and weighing after each addition of gas. The standard taper joint at J is used for this purpose.

Discussion

Heterogeneous Surfaces.—It was observed previously that log–log plots for nitrogen isotherms on many different surfaces were so nearly parallel to one another that specific effects of the surface did not appear to have any influence on the adsorption after the first layer is completed. Additional study has been made of this point. Using only nitrogen isotherms whose log–log plots are linear up to a relative pressure near 0.8 (showing absence of capillary condensation in pores less than 100 Å. in diameter) we find that for the majority of the available isotherms the previous conclusion is essentially correct—that once the first layer is completed subsequent adsorption is not related to the type of atoms in the primary surface or to the structure of the surface lattice. Occasionally an isotherm is found whose log–log plot does not give the expected slope but this is so rarely observed that when it occurs the deviation is attributed to experimental error rather than to surface effects. In every case where such an isotherm is found we have found other published isotherms for very

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(9) Corning No. 39570 sealing tubes with fritted discs, 13 mm. diameter, medium porosity.

similar surfaces whose log–log plots do have proper slopes.

Comparison of log–log plots for scores of nitrogen isotherms does show a small deviation in the slopes. The value of s in Eq. 1 is found to vary from 2.5 to 2.9. The variations, however, seem to be random rather than related to the solid substrate. Isotherms for similar surfaces, *e.g.*, SiO_2, TiO_2, C, etc., from different laboratories may give plots of slightly different slope but if different surfaces are compared by data from a single laboratory the various log–log plots are closely parallel to one another. At present no definite conclusion can be drawn as to the cause of these deviations but one possible reason lies in the determination of the dead space of the sample bulb. This correction is not important at the low relative pressures of the first layer region but it becomes increasingly more important as the saturation pressure is approached. A small error in it might cause appreciable error in the computed multilayer adsorption at high relative pressure. Another possibility is in the determination of p_0, but since practically all workers today use vapor pressure thermometers this does not seem to be a probable error.

In any event it seems safe to conclude that when a log–log plot of the amount adsorbed *vs* log p_0/p does not give a straight line of approximately normal slope for that adsorbate, either there is experimental error or else there is not unrestricted free surface adsorption. Consequently the construction of a log–log plot from the data of the multilayer region is useful in interpretation of isotherms. In making the plot any quantity that is proportional to the amount adsorbed may be used. In working with published curves it is convenient to plot the height of the isotherm (in mm.) rather than converting to the actual amount adsorbed. The following types of information have been obtained from studies of log–log plots:

1. Capillary condensation in large pores or at contact points between powder particles is detected by deviations of isotherm points from the straight line at higher relative pressures.[3] Many instances of such capillary effects have been noted for samples whose isotherms appear to be for a free surface (Type II) and which show no hysteresis on desorption except at very high relative pressures. Deviations from the linear log–log plot provide a more convenient test of capillarity than the use of desorption hysteresis and eliminate the need for saturating the sample near p_0, a laborious operation at best.

2. The log–log plot may be used to determine the point at which a liquid meniscus first forms in pores and capillary condensation begins. When this occurs the experimental points begin to fall above the straight line plot. The size of pores at the start of capillary condensation then may be computed by application of the Kelvin equation, taking into account the depth of the free surface film at this point, as has been done in pore size analyses from desorption isotherms.[10,11]

3. When a portion of the surface lies in very small pores that fill by the time a first layer is formed on the free surface the apparent surface area may be too great, since the amount adsorbed by capillarity is included in the V_m measurement. A log–log plot may be used to detect small capillaries by showing a curved rather than straight line or a straight line of too low a slope. The isotherm of a finely divided carbon black, Carbolac I, illustrates this effect.[3] The log–log plot of the isotherm determined by Emmett and Cines[12] is linear but with far less slope than the normal nitrogen isotherm. Using their data and the number of statistical layers for a normal isotherm on a free surface it was shown that about 142 ml. of nitrogen is adsorbed per gram in the small pores and 104 ml. in the first layer on free surface not in these pores.[13]

4. The fact that isotherms for a given adsorbate all give essentially the same slope for a log–log plot makes it possible to compute surface areas by the adsorption at any given relative pressure in the multilayer region.[14] The number of statistical layers, n, may be computed from any nitrogen isotherm by dividing the amount adsorbed at given relative pressures by the BET value for V_m. Conversely, the ratio V/n gives directly V_m.

Average values for n at various relative pressures are given in Table I. Account is taken of the small deviations in slopes of the log–log plots, so that such a plot for the n-values gives a line of average slope. These values differ slightly from those given by Shull,[15] which were based upon earlier and more scanty data. The present ones may be made more reliable when the cause of the differences in isotherms of various workers is determined and all results brought into more exact agreement. A log–log plot of the n-values is shown in Fig. 3.

TABLE I

NUMBER OF STATISTICAL LAYERS OF NITROGEN ADSORBED AT SELECTED RELATIVE PRESSURES

p/p_0	n	p/p_0	n
0.2	1.26	0.6	1.90
.3	1.40	.7	2.17
.4	1.54	.8	2.57
.5	1.70	.9	3.38

To compute V_m the adsorption at an arbitrarily selected relative pressure of 0.50 is divided by the n-value, 1.70. This pressure is selected because most isotherms show no filling of pores at this low

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(10) E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).

(11) C. Pierce, *J. Phys. Chem.*, **57**, 149 (1953).

(12) P. H. Emmett and M. Cines, *J. Phys. Chem.*, **51**, 1329 (1947).

(13) It was brought to our attention by Dr. W. V. Kotlensky of the Jet Propulsion Laboratory, Pasadena, Calif., that there is an arithmetical error in the small pore volume of 0.29 ml. per g. previously reported. An adsorption of 142 ml. N_2 is 0.178 g. which at normal liquid density gives a pore volume of 0.22 ml. This agrees with the pore volume found by Dr. Kotlensky by helium displacement.

(14) Isirikyan and Kiselev[2] have suggested essentially the same idea for nitrogen isotherms on graphite. They have shown that all isotherms for such surfaces may be reduced to a unified specific isotherm giving the amount adsorbed at any relative pressure by 1 m.^{2} of graphite surface, so that a single adsorption point may be related to the amount of surface. As discussed later, the specific surface isotherm given by Isirikyan and Kiselev appears actually to be for 0.8 m.^{2} rather than for 1 m.^{2}.

(15) C. G. Shull, *J. Am. Chem. Soc.*, **70**, 1405 (1948).

a pressure. Tests of scores of isotherms show almost uniformly good agreement between the V/n and the BET value for V_m. When the agreement is not good, as for Carbolac I, the presence of small pores is suspected.

Normally one does not need to use the V/n ratio since the isotherm data may be used to construct a BET plot. The method is useful, however, for isotherms which do not give a linear BET plot[16] up to 0.30 p_0 and for the interpretation of the isotherms of uniform surface graphites, as discussed in a later section. Frequently the V/n ratio is helpful in getting V_m from published isotherms without constructing a BET plot.

The nitrogen n-values of Table I are not strictly applicable to other adsorbates or to nitrogen at temperatures other than its boiling point. The slopes of the log-log plots for many adsorbates are, however, sufficiently close to that for nitrogen plots that one may use the n-value of 1.70 for a relative pressure of 0.5 to get a good approximation to V_m for isotherms of many adsorbates. Comparison of the log-log plot with one for the nitrogen n-values will show when the two are sufficiently alike in slope to permit use of the nitrogen n-value.

5. Effects of chemisorption upon subsequent physical adsorption may be detected by abnormalities in the log-log plot. An example of this was noted in the ethyl chloride isotherm of anatase. The sample had been degassed at 100° to avoid removal of surface-OH groups. The isotherm after this treatment gave a curved log-log plot. It was suspected that the -OH groups were responsible. This was confirmed by degassing at 350°. After this an isotherm of normal slope was obtained. Removal of the -OH groups had only a small effect upon the nitrogen isotherm for the same sample.

Uniform Surfaces.—Reported isotherms[2,8] for Sterling MT (3100°) indicate that this graphite has a very uniform surface. It was, therefore, selected for study of the effects of a uniform surface upon adsorption in the multilayer region.

In the development of Eq. 1 it was assumed that the adsorbing surface is an infinite plane of uniform activity, so that adsorbate is held with equal strength at all sites. Both Halsey[5] and Hill[6] recognized that with such a model, adsorption in the multilayer region should not have the usual continuous increase with pressure but rather the isotherm should show steps for the successive layers, corresponding to sudden changes in the attractive force in passing from one layer to the next. A normally smooth isotherm might be expected only when the surface is non-uniform and there is a distribution of attractive forces among the sites. This distribution should carry over into succeeding layers and wash out the discontinuities between successive layers. This is what is found for non-uniform surfaces.

Contrary to the predictions of the theory, most isotherms on uniform surfaces do not have steps for successive layers but rather are smooth curves just like those obtained for heterogeneous surfaces. Benzene,[2] n-hexane,[2] nitrogen and ethyl chloride at 0° all give smooth isotherms on Sterling MT, with no indication of a second layer step. Krypton and argon do show sharp steps for the second layer[5] when adsorbed at −195 and −209°, respectively, but these steps may be regarded as somewhat anomalous since the temperatures are below the normal freezing points of the vapors and there is some uncertainty as to whether the film is liquid or solid. Recently Prenzlow and Halsey[5] have observed second layer steps for adsorption of oxygen and nitrogen on graphite at −209°, which is quite close to the normal freezing points of the vapors.

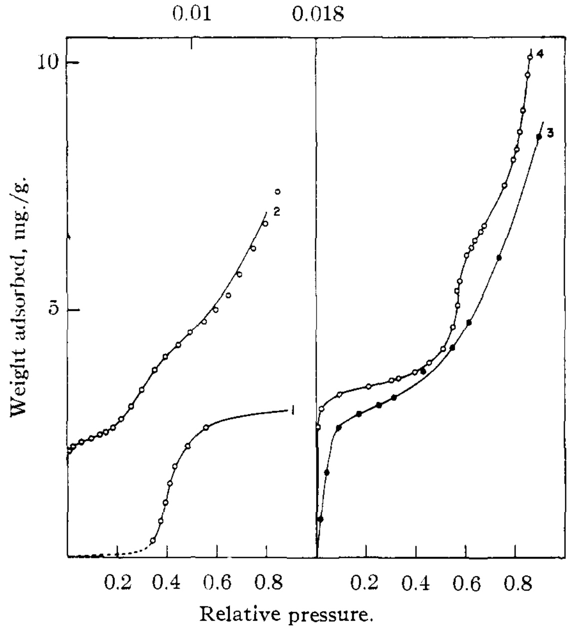

Fig. 2.—Isotherms for Sterling MT(3100°): (1) Low pressure region for ethyl chloride at −78°. The relative pressures are given by the scale at the top. (2) Nitrogen at −195°: solid curve, our data; circles, data from Isirikyan and Kiselev,[2] computed from their specific isotherm and their BET area of 7.65 m.^{2}/g. for MT. (3) Ethyl chloride at 0°: this isotherm was measured gravimetrically. (4) Ethyl chloride at −78°.

Isotherms for ethyl chloride at 0 and −78° and nitrogen at −195° on Sterling MT are shown in Fig. 2. Log-log plots of the nitrogen and the ethyl chloride 0° isotherms are given in Fig. 3. These data, in conjunction with those of Isirikyan and Kiselev,[2] for similar graphite surfaces, illustrate some general properties of adsorption on a uniform surface:

1. The initial shape of the ethyl chloride isotherm at −78° indicates that the sample has a highly homogeneous surface. Earlier, a similar isotherm was determined for Graphon,[17] which was the most uniform surface known at the time. Comparison of the MT and Graphon isotherms indicates that the MT surface is more uniform, for its isotherm has no initial concave portion while that for Graphon does. The isosteric net heat of adsorption on MT, shown in Fig. 4, does not have an initial drop like the one for Graphon. Insofar as can be judged from the present isotherm and the

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[16] See D. S. MacIver and P. H. Emmett, *J. Phys. Chem.*, **60**, 824 (1956).

[17] J. Mooi, C. Pierce and R. N. Smith, *J. Phys. Chem.*, **57**, 657 (1953).

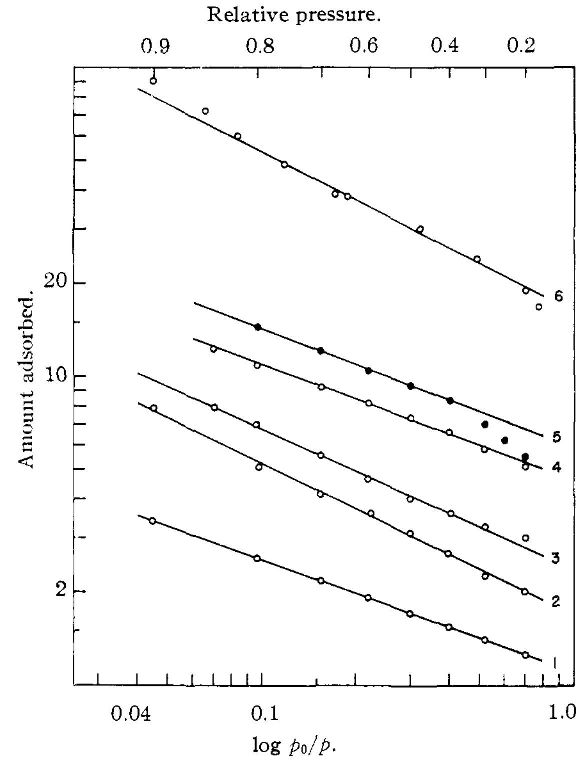

Fig. 3.—Log-log plots for adsorption in the multilayer region; the scale at the top shows relative pressures. (1) Number of statistical layers, *n*, see Table I. (2) Benzene on graphite, data of Isirikyan and Kiselev.[2] (3) Ethyl chloride at 0° on Sterling MT(3100°). (4) Nitrogen on anatase from lot used by Jura and Harkins.[7] (5) Nitrogen on Sterling MT(3100°). The adsorption is given for a 2-g. sample, to facilitate plotting. (6) Benzene on quartz with hydrated surface. The specific surface is 6 m.^{2}/g. Data of Isirikyan and Kiselev, *Doklady Akad. Nauk, USSR*, 119, 731 (1958).

heat curve Sterling MT (3100°) has *no* heterogeneous portion of the surface.

The differences between Graphon and samples similar to Sterling MT (3100°) have been noted by Graham[18] and by Isirikyan and Kiselev.[2] All agree that the Graphon surface has more heterogeneity than the other graphites prepared from carbon blacks. According to Graham 1.25% of the Graphon surface sites are strong, while another graphite made from P33 has only 0.1% of the surface in strong sites.

A possible explanation for the heterogeneity found in Graphon surfaces lies in the structure of the particles. Graphon is prepared by heating Spheron 6, a previously pelletized carbon black. The pellets are formed by agitating "fluffy" carbon black so that many particles flock together. This is done to facilitate handling. When the sample is graphitized the pellet structure remains, so that the ultimate particle is an aggregate of many finer particles. Consequently there are many contact points where the particles touch one another. Each such contact point constitutes a strong site where an adsorbate molecule can touch two walls and where capillary condensation can occur. Heats of immersion measurements with benzene[19] have shown that Graphon has a pore structure that can be accounted for by an aggregation of spherical particles.

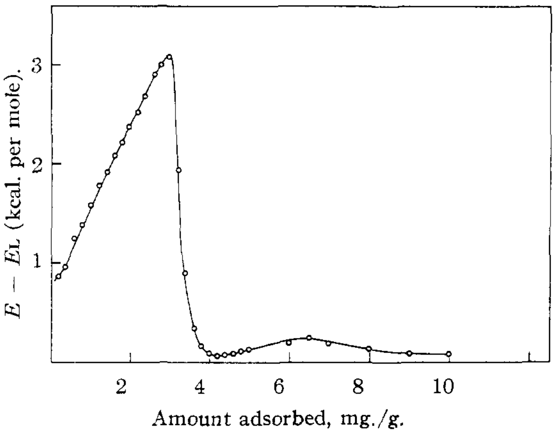

Fig. 4.—Isosteric net heat of adsorption for ethyl chloride on Sterling MT(3100°).

The isotherms of Isirikyan and Kiselev and those in Fig. 2 illustrate the ways in which lateral interactions may affect adsorption isotherms when the surface is uniform and there are no preferred adsorption sites. Nitrogen, *n*-hexane and ethyl chloride all have isotherms that are convex to the pressure axis prior to completion of the first layer. It appears that the adsorbate–adsorbate forces are strongest for ethyl chloride, since its isotherm is most nearly vertical below the V_m point. Its heat of adsorption curve shows the greatest interaction energy. Benzene does not appear to have any measurable lateral interaction and its isotherm is of the BET type, concave to the pressure axis throughout the first layer region. The rise below V_m is not vertical for any of the adsorbates investigated, as would be the case for a true "phase change."

Comparison of the 0 and −78° isotherms for ethyl chloride shows that as the temperature is raised and thermal agitation increases the effects of lateral interactions become less pronounced.

2. The ethyl chloride isotherm at −78° has a sharp step for adsorption in the second layer and quite a flat tread between the first and second layer steps. This is the most pronounced example yet noted of stepwise adsorption in a truly liquid film, since the temperature is some 60° above the freezing point. At 0° the step no longer shows and a log–log plot is linear throughout the multilayer region, up to the start of condensation between particles. The ethyl chloride isotherm on Graphon showed no indication of a second layer step at any temperature. None of the other adsorbates shows a second layer step on MT. These data indicate that stepwise adsorption is highly sensitive to three factors, (1) uniformity of the surface, (2) strong lateral interaction between adsorbate molecules, and (3) a sufficiently low temperature that thermal agitation does not smear out the small energy differences that give rise to the steps. Consequently it is not surprising that such steps

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(18) D. Graham, *J. Phys. Chem.*, **61**, 1310 (1957); **62**, 1210 (1958).

(19) C. Pierce, J. Mooi and R. E. Harris, *J. Phys. Chem.*, **62**, 655 (1958).

are infrequently observed. From the isotherm at 20° and the lateral interaction effects shown in the heat of adsorption curve[2] one would predict that *n*-hexane probably would give a second layer step if the isotherm were determined at a temperature below −30 or −40°.

It is surprising that the small difference in heterogeneity of the two surfaces would permit the ethyl chloride isotherm to show a step on the MT surface and not on the Graphon. If Graham's figures are correct, and they seem in line with Graphon isotherms, one would expect the −78° ethyl chloride isotherm on Graphon to show some indication of a second layer step.

3. The nitrogen isotherm for MT exhibits the sharp rise at a relative pressure near 0.4 that is characteristic for isotherms of nitrogen on uniform surface graphites. Argon at −195° has a similar hump in the isotherm. This phenomenon was first reported by Joyner and Emmett[20] for one of the early Graphon samples. At the time it was attributed to the start of a second layer step but analysis of the isotherm by a log–log plot suggests an entirely different explanation. Plots for the isotherm on MT and on an anatase sample are given in Fig. 3. The two are closely parallel above a relative pressure of 0.4. Below this pressure the points of the MT isotherm fall below the straight line, gradually approaching it as the pressure rises.

The fact that the plots for graphite and anatase isotherms are parallel shows that the number of statistical layers on the two surfaces at a given relative pressure must be the same. When the V_m value for anatase is computed by a BET plot and by the V/n ratio the two agree closely. This is not true for the MT isotherm. The V/n ratio gives 2.69 mg./g. for V_m while a BET plot gives 2.20 mg./g., which is, as usual, in close agreement with a visual estimate from the inflection point of the curve. If the BET value of V_m is used to compute the number of statistical layers a plot of these values gives a line with far too steep a slope. We conclude, therefore, that the true V_m is the value obtained by the V/n ratio from adsorption in the multilayer region. This gives a surface area of 9.4 m.^{2}/g. for Sterling MT (3100°) instead of 7.65. Thus, for samples whose isotherms have the abnormal hump near 0.4 p_0, the BET area is only about 80% of the true area.

It is not implied that there is any defect in the BET method for computing V_m. The value found is in conformity with the shape of the isotherm and is very close to the inflection point at which the first layer is completed. The deviation of isotherm points from the log-log plot below 0.4 p_0 suggest rather that at apparent completion of the first layer the nitrogen is not packed to normal film density, with a coverage (σ) of 16.2 Å.^{2}/molecule. At this point of the MT isotherm σ is, instead, 20.2 Å.^{2}/molecule. As the pressure is increased further adsorption takes place in two ways, by filling in of the first layer until normal density is reached and by start of the second layer. When a relative pressure of 0.4 is reached the film is normal and thereafter multilayer adsorption proceeds as on any other surface. It is interesting to note that Isirikyan and Kiselev,[2] using an entirely different approach, have also concluded that the first layer adsorption of nitrogen on a graphite surface is initially localized with σ about 18 Å.^{2}/molecule.

All of the graphitized carbon blacks show this abnormality in the nitrogen isotherm, even those with somewhat heterogeneous surfaces, such as Graphon. From a practical point of view this is unfortunate, for such blacks have been very widely used for adsorption studies and all of the published areas are based on 16.2 A.^{2} for the N_2 molecule. Consequently all the published areas are too small and should be increased by about 25%. The specific isotherms given by Isirikyan and Kiselev are not for 1 m.^{2} of surface but rather for *ca.* 0.8 m.^{2}, since all are based on abnormal nitrogen isotherms.

Independent confirmation of the preceding conclusions is found in comparing isotherms for benzene on graphite and silica surfaces, using data of Isirikyan and Kiselev.[2] Both isotherms are the BET type, concave to the pressure axis below V_m. The log–log plots for the two, shown in Fig. 3, have the same slope, showing that the *n*-values are identical. This means that σ must have the same value on the two surfaces. Using the nitrogen areas, Isirikyan and Kiselev find σ to be 40 A.^{2} on the graphite and 49 A.^{2} on the silica sample. Correcting the area of the graphite sample as described above brings the two into agreement, with a value of 50 A.^{2} for the graphite surface.

A study of scale molecular models for the benzene molecule indicates that 50 A.^{2} is a reasonable coverage for an adsorbed molecule. Arrangements of models were made to give each molecule six symmetrically placed neighbors. If the spacing is such as to allow each molecule to rotate in the plane without disturbing any neighbor, the area per molecule is found to be 49 A.^{2}. An area of 40 A.^{2} required that the models be so placed that the H-atoms from separate molecules would interfere with one another, so that no molecule had free rotation alone. The looser arrangement would seem to be more probable, since it permits maximum entropy for the adsorbed molecules. Incidentally the close agreement found for areas deduced from the models and from adsorption isotherms provides further confirmation that in its normal packing the adsorbed nitrogen molecules covers 16.2 A.^{2}.

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