Unfortunately the case of iodine is suspect inasmuch as Shaffer[2c] states that the experiment was made in the presence of iodide ions which would be expected to form complexes with the several tin ions and hence might well catalyze the reaction by lowering the potential hump. The auricyanide however, is practically free from suspicion on this score.

Experimental

The space limitations of THIS JOURNAL do not permit a detailed presentation of the experimental details so only the high points can be presented. The ceric sulfate solution used was prepared by Dr. G. R. Sherwood. The solution, when placed in an absorption cell 5-cm. wide, showed no absorption lines in the red end of the spectrum, thus indicating the absence of praseodymium and neodymium and indicating the high probability that other rare earths were also absent.

The potential of the auri-aurocyanide system cannot be satisfactorily determined in acid solution by the potentiometric method. Accordingly, it was determined roughly by finding out which reversible reducing agents in 1 to 2 *N* sulfuric or hydrochloric acid were oxidized by auricyanide and which were not. Auricyanide was found to oxidize iodide ion and leuco-indigodisulfonate whereas it failed to oxidize diphenylamine, toluhydroquinone, ferrous sulfate and bromide ions. It was concluded that the potential lies between 0.53 and 0.59 volt.

The experimental differentiation between fast and slow oxidations of stannous ions was carried out essentially in the absence of oxygen and, in the case where molybdicyanide was the oxidizing agent, with the complete exclusion of light. The results are shown in Table I in which the data marked with asterisks were obtained in this laboratory. The remaining data were taken from Shaffer's publications except for certain potential values which were chosen with care from the literature. Only in the case of the pure ceric sulfate was the sulfuric aid more concentrated than 4 *N*. In this case it was about 10 *N*. Comparable concentrations were used in all experiments.

Summary

1. Experiments were made which showed whether stannous ions in the absence of oxygen reacted rapidly or slowly in dilute sulfuric acid solution with ferric phenanthroline ion, potassium molybdicyanide, potassium auricyanide, cupric sulfate and highly purified ceric sulfate.

2. The reduction potential of the auricyanide–aurocyanide system in acid solution was determined approximately by observing whether or not reduction occurred with a series of reducing agents of graded potentials. It was found to lie between 0.53 and 0.59 volt in dilute acid solution.

3. The above facts were discussed in relation to the opposing oxidation–reduction theories of Shaffer and Weiss and it was shown that if Shaffer's theory were extended by introduction of the concept of potential humps it offers a satisfactory explanation of the observed facts. Weiss's suggestion that electrostatic repulsion is a sufficiently powerful influence to determine whether a given ionic oxidation–reduction reaction will be fast or slow is not borne out by the experimental facts.

DETROIT, MICH. RECEIVED MAY 6, 1946

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AND THE RESEARCH LABORATORY OF GODFREY L. CABOT, INC.]

Heats of Adsorption on Carbon Black. I

BY R. A. BEEBE,[1] J. BISCOE,[1] W. R. SMITH[2] AND C. B. WENDELL[2]

The differential heats of adsorption on a number of commercial carbon blacks are being determined calorimetrically in an attempt to find a correlation between the state of surface of these blacks and their unique efficiency in rubber reinforcement. With the problem of reinforcement in mind, interest would naturally center on heat measurements with various olefins or diolefins as adsorbates. The results of such experiments, which are now in progress, will be reported in a subsequent publication.

Before investigating the hydrocarbon adsorbates, it was decided to make a series of measurements with nitrogen, oxygen and argon at liquid nitrogen temperature. It was felt that work with these elementary gases, especially nitrogen, would not only give information about any qualitative differences in the carbon black surfaces but that, in addition, it would yield data of general significance in the field of physical adsorption. This plan of investigation would have two possible points of advantage over many previous calorimetric measurements of heats of adsorption. First, the recently developed theory of physical adsorption due to Brunauer, Emmett and Teller[3] makes it possible to estimate the value of v_m, the volume of adsorbate necessary to fill the monolayer, and hence it is possible to relate the differential heats of adsorption to the fraction of surface covered. Second, although complex in physical structure and chemical constitution, the carbon blacks have highly reproducible surfaces and the large body of information concerning particle size and crystal structure of the blacks further enhances their value for use in fundamental adsorption studies.[4]

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(1) Amherst College, Amherst, Mass.

(2) Godfrey L. Cabot, Inc., Boston, Mass.

(3) (a) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 310 (1938); (b) following common practice, this will be referred to as the B. E. T. theory.

(4) (a) Emmett and DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941); (b) Smith, Thornhill and Bray, *Ind. Eng. Chem.*, **33**, 1303 (1941); (c) Wiegand and Ladd, *Rubber Age*, **50**, 431 (1942); (d) Biscoe and Warren, *J. Applied Phys.*, **13**, 364 (1942).

TABLE I

ANALYTICAL PROPERTIES OF CARBON BLACKS

Sample	Diam.,[a] Å.	Area,[b] sq. m./g.	Volatile content, %	D. P. G.,[c] mg. ads./g.	D. C. resist., ohm/cm.	L_C, Å.	L_A,[d] Å.
Spheron Grade 6 (MPC)	285	110	5.0	7.6	28.3	12.7	20.0
Spheron Grade 6, "devol."	285	120	<1	1.1	0.8	14.9	28.0
Graphon	300	85	<1	0.8	.5	40.0	65.2
Sterling S (SRF)	600	24	<1	1.7	.8	..	..
Sterling L (HMF)	500	30	<1	0.5	.5	..	..

[a] Modal diameter from electron microscope measurements. [b] From nitrogen isotherm. [c] Reference 7. [d] Reference 4d.

While the results presented in this paper with the elementary gases as adsorbates at −195°[5] are of more immediate interest in the general field of adsorption, they do nevertheless yield information of significance to the rubber reinforcement problem even though it was anticipated that the bulk of such information would come from the investigation with hydrocarbon adsorbates at higher temperatures.

Experimental

Carbon Blacks.—Five carbon blacks have been selected for the present investigation. Three of these are samples of commercial blacks made by Godfrey L. Cabot, Inc., and the others were specially prepared for this study. Their pertinent analytical properties are reported in Table I. The Spheron Grade 6 is designated in the rubber tire industry as a medium processing channel black (MPC). It is a fully reinforcing black with a modal diameter of 285 Å. Its "volatile content"[6] as determined by heating to 927° in the absence of air is 5% by weight. This is largely chemisorbed oxygen and hydrogen. The chemisorbed oxygen which is confined largely to the surface is evolved as carbon monoxide and carbon dioxide. This process of "devolatilization" has little effect on the particle size or surface area of the carbon. However, the effect of these surface oxides on the adsorption of basic rubber accelerators, such as diphenyl guanidine, from benzene solution[7] is quite marked, the adsorption being reduced sevenfold by their removal. Removal of the surface oxides also lowers the contact resistance between black particles as may be judged from the sharp drop in the D. C. resistance of the black as measured at a pressure of 150 lb./sq. in.

Heating MPC black to 3200° does not significantly alter its particle size or surface area, as may be judged from the data on "Graphon," a commercial form of partially "graphitized" carbon black. The chemical nature of the surface of the "graphitized" black as judged from diphenylguanidine adsorption and electrical conductance is quite similar to the "devolatilized" sample.

The X-ray diffraction patterns of samples of Spheron Grade 6, "devolatilized" Grade 6, and Graphon have been reported by Biscoe and Warren.[4d] The dimensions, L_C and L_A, of the parallel layer groups within the carbon black particle have been computed from these patterns and are included in Table I. They are essentially the same for the Spheron Grade 6 and the "devolatilized" sample. In other words, removal of the chemisorbed gases by heating to 927° has not significantly altered the physical structure of the carbon black particle. However, heating to about 3200° has markedly altered the internal structure of the particle as shown by the data for Graphon. In this instance the dimensions L_C and L_A of the parallel layer groups have increased three-fold and the orientation within the parallel layer groups is more ordered than in the original Grade 6 sample. The Spheron Grade 6, Grade 6 "devolatilized" and partially "graphitized" Grade 6 (Graphon), present an interesting series. While the particle size of all three is essentially the same, the nature of the surface and internal structure is varied.

Two commercial furnace blacks, Sterling S and Sterling L, have also been included in the present study. These blacks are considerably coarser than the channel blacks. The semi-reinforcing properties of the Sterling S sample (SRF) could be presumably attributed to particle size. The Sterling L sample (HMF) is intermediate in reinforcing ability as may be judged from the data of Table II. This characteristic of high modulus furnace (HMF) blacks has also been confirmed by tire road wear tests.[8] It is not improbable that the reinforcing properties of HMF blacks are associated with the state of the surface.

The stress-strain properties of all the blacks compounded in a standard natural rubber tread stock is reported in Table II. The values reported are those at optimum cure. The stress-strain properties of Spheron Grade 6 and "devolatilized" Grade 6 are essentially the same. This is in accord with the view that the volatile or chemisorbed surface oxygen does not play a fundamental role in reinforcement, its effect being largely one of retarding the rate of sulfur vulcanization.

The reinforcing properties of the "graphitized" channel black (Graphon) have been markedly altered. The "stiffening" effect of the black as judged from modulus at 300% elongation has

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(5) Under experimental conditions, with different batches of commercial liquid nitrogen used in the bath, the temperatures ranged from −194.5 to −195.1° as measured with an oxygen thermometer.

(6) Johnson, *Ind. Eng. Chem.*, **20**, 904 (1928).

(7) Amon and Estelow, *ibid.*, **24**, 579 (1932).

(8) Drogin, *Rev. gen. caoutchouc*, **23**, 47 (1946).

TABLE II

RUBBER PROPERTIES OF CARBON BLACKS[a]

All cures at 135°, data given for rubber of optimum cure.

Sample	Tensile strength lb./sq. in.	Modulus, 300 elong., lb./sq. in.	Abrasion[a] loss
Spheron Grade 6 (M PC)	4300	1720	397
Spheron Grade 6 "devol."	4300	1940	390
Graphon	3800	230	600
Sterling S (SRF)	3100	1390	646
Sterling L (HMF)	3500	1820	577

[a] Recipe:—

Smoke sheet	100 parts	Pine tar	3 parts
Black	45 parts	Stearic acid	4.0 parts
Zinc oxide	5 parts	Agerite Hipar	1.0 parts
Sulfur	3 parts	Captax	0.9 parts

[a] Abrasion loss = cc. stock abraded per revolution × 10^6. Determined with Akron standard mold angle abrader; wheels at 15° and 6 kg. load. See Memler, "Science of Rubber," Reinhold Publishing Corp., New York, N. Y., 1934, p. 599.

been drastically reduced as has the abrasion resistance.

While the tensile strength of the reinforced tread stock containing Graphon has been lowered beyond experimental error (±200 lb./sq. in.) in the present instance, other samples of this material[4b] have been studied which do not show any essential difference in this respect. It is generally found that tensile enhancement by carbon black is a function of particle size of the pigment and is not primarily associated with the state of the surface. It is true, for the sample studied here, that both the electron microscope and surface area measurements indicate a somewhat larger particle after "graphitizing," a phenomenon which could be associated with a slight sintering action during the heat treatment.

The stress-strain properties of the two furnace black samples are quite characteristic and indicate the relative positions of these materials as reinforcing pigments.

Apparatus.—Except for the calorimeter, the apparatus was similar to that generally in use for nitrogen adsorption measurements of the type required for surface area measurements by the method of Brunauer, Emmett and Teller.[3]

The calorimeter, one form of which is shown in Fig. 1, was a modified form of the calorimeters previously developed in the Amherst Laboratory and described in earlier publications.[9] The design was altered to make it easier to exchange samples of adsorbent. The most important changes were (a) increase in the diameter of the lower part of the Pyrex glass inlet tube A. (b) the use of a removable platinum cylinder B containing the carbon black and (c) the inclusion of a heating coil of insulated resistance wire CC′ (embedded in the carbon black adsorbent) making possible the electrical calibration of the calorimeter for heat capacity (shown in cross section of Fig. 1). As in previous work,[9a] the calorimeter was so constructed that the incoming gas would first enter the adsorbent mass through a small vertical metal tube D at the center of the platinum calorimeter containing the carbon black (shown in cross section in Fig. 1) and then would diffuse horizontally through small holes bored through this vertical tube at various levels. This would eliminate as far as possible any effect due to non-selective adsorption.[9b] A glass plug not shown in Fig. 1 was inserted to "kill" the free space inside the adsorption system above the Pyrex–Kovar–platinum seal. In the largest calorimeter used, the outer stationary platinum cylinder E was 2 cm. in diameter and 7 cm. long,

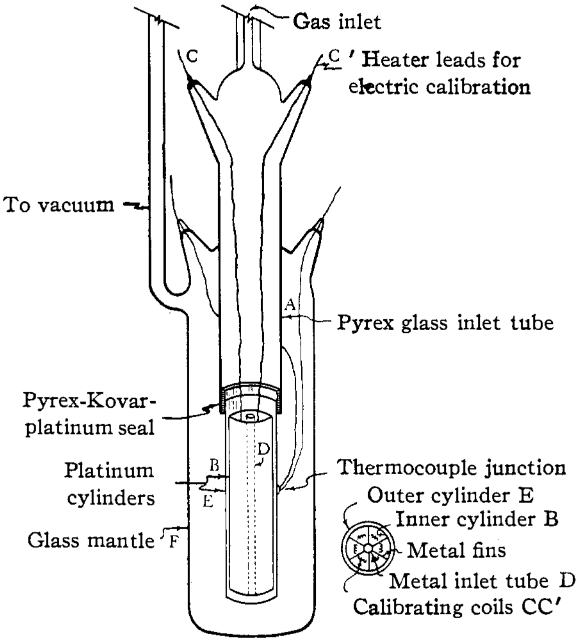

Fig. 1.—The calorimeter.

The early experiments reported in this paper were carried out with a vacuum jacket in the space between the outer platinum cylinder E and the glass mantle F. However, it was found that there was considerably more heat loss than had been observed with previous models of the calorimeter doubtless due in part to the larger mass of the glass inlet tube A. Moreover, it was recognized that the heat loss due to radiation would be even greater in the work contemplated with hydrocarbons at 0°. As a result it was decided to modify the procedure to use a gas-filled outer jacket. It may be said here that in duplicate runs at −195°, using the vacuum jacket in the one case and the gas filled jacket in the other, no significant difference was found in the differential heat curves. It was found by experience that helium or a helium–nitrogen mixture served best in the outer jackets of our particular calorimeters; a gas pressure of 7–8 mm. was used.

The heat, Q, evolved in the adsorption process,

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(9) (a) Beebe and Orfield, THIS JOURNAL, **59**, 1627 (1937); (b) Beebe and Dowden, *ibid.*, **60**, 2912 (1938); (c) Beebe and Stevens, *ibid.*, **62**, 2134 (1940)

was determined from the galvanometer deflection *vs.* time curve, using the relation[10]

$$Q = Cy = C\left[x - k\int_0^t x\mathrm{d}t\right]$$

where y is the galvanometer deflection that would have been observed if there had been no heat loss, x is the observed deflection, and k is the constant appearing in the equation for Newton's law of cooling. The constants C and k were both determined from the electrical calibration curve, k being equal to the slope of the straight line formed by plotting log x *vs.* t, for times after the current had been shut off. $\int_0^t x\mathrm{d}t$ was found by planimeter.

In the course of the work it was recognized that there were several potential sources of error. These were in general estimated to be small; and no one of them appeared to exceed a few per cent. The sources of error considered were (a) deviation from the gas laws, (b) loss of heat from lead wires of the heating element during electrical calibration, (c) heat of compression of the unadsorbed gas for later increments,[11] (d) variations in the temperature of the reference junction which was lagged by being soldered to a copper block immersed in the liquid nitrogen bath (not shown in Fig. 1). Effect (d), which showed up as a minor variation in the time-temperature curves, was more marked in the liquid nitrogen bath than in the liquid oxygen baths previously used.[9] It was estimated that the net effect of all those minor sources of error, not corrected for, could not exceed ±5% and was probably considerably less except in a few especially unfavorable cases. It is emphasized that while these errors can account for the failure of the experimental points to fall on a smooth curve (Figs. 3–8), they are insufficient to account for any major variations in the differential heats in a given run or for marked differences in the shapes of the differential heat curves with different blacks.

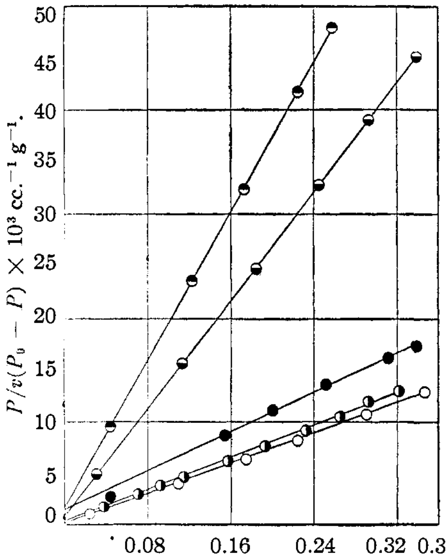

Fig. 2.—B.E.T. plots, nitrogen at −195°; Spheron Grade 6 ◑; Spheron Grade 6 "devolatilized" ○; Graphon ●; Sterling S ◓; Sterling L ◒;

Results

Altogether 23 successful heat runs have been carried out with the elementary gases at −195°. The experimental results of representative runs are plotted in Figs. 2–8. In Fig. 2 are given the B.E.T. plots[3b] for nitrogen on the five blacks which have been studied. Assuming that the area occupied by the nitrogen molecule on the surface is 16.2 sq. Å., the values have been calculated for the specific surface areas given in Table I. Figures 3–6 give the results of heat runs with nitrogen adsorbate at −195°. In Fig. 3 are given the results of heat runs on Spheron Grade 6 black. In selecting data for this plot, results have been used with three different samples measured in three different calorimeters of different sizes and somewhat different design. Figures 4, 5 and 6 give the experimental results with "devolatilized" Grade 6, with Graphon, and with the furnace blacks, respectively.

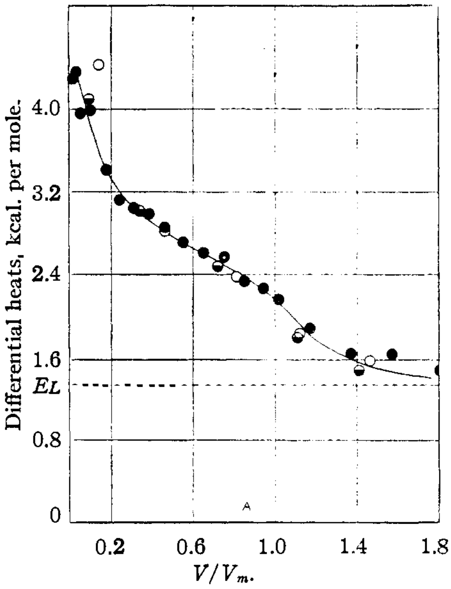

Fig. 3.—Heats of adsorption at −195°; nitrogen on Spheron Grade 6: run 8 (small cal.) ○; run 14 (medium cal.) ◒; run 16 (large cal.) ●.

In heat runs on the same sample of Spheron Grade 6, the relative behaviors of nitrogen and oxygen are compared in Fig. 7. Finally a single run with argon is represented in Fig. 8.

In all these plots v_m, the volume of adsorbate required to fill the monolayer, has been calculated

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[10] See for example J. M. Cork, "Heat," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1933, p. 58.

[11] Ward, *Proc. Roy. Soc.* (London), **133A**, 506 (1931).

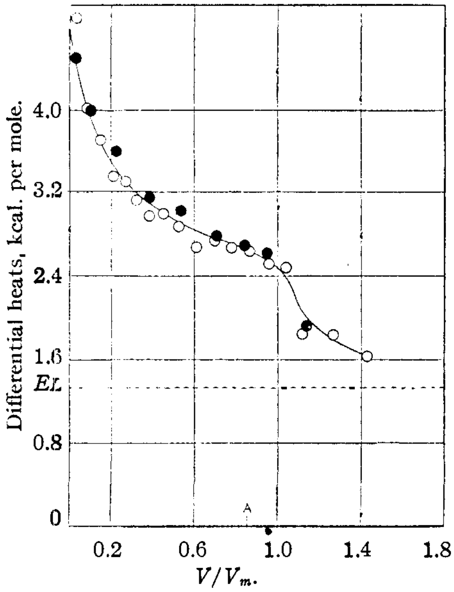

Fig. 4.—Heats of adsorption at −195°; nitrogen on Spheron Grade 6 "devolatilized"; run 20 (large cal.) ○; run 26 (medium cal.) ●.

by the standard B.E.T. method, using the p and v data obtained simultaneously with the heat measurements. In Figs. 3–8 the line marked A represents the point at which $v/v_m = 1$ when v_m is calculated by the modified B.E.T. equation due to Anderson.[12] It is to be noted that the Anderson equation gives v_m values which are from 8 to 15% higher than the simple B.E.T. values, with the result that v/v_m is correspondingly lower.

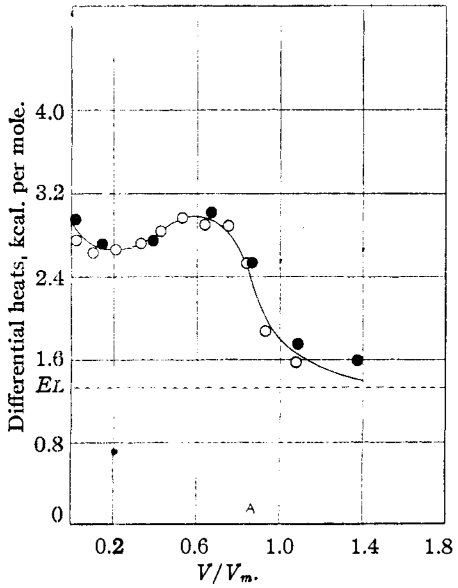

Fig. 5.—Heats of adsorption at −195°; nitrogen on Graphon: run 18 (helium jacket) ●; run 19 (vacuum jacket) ○.

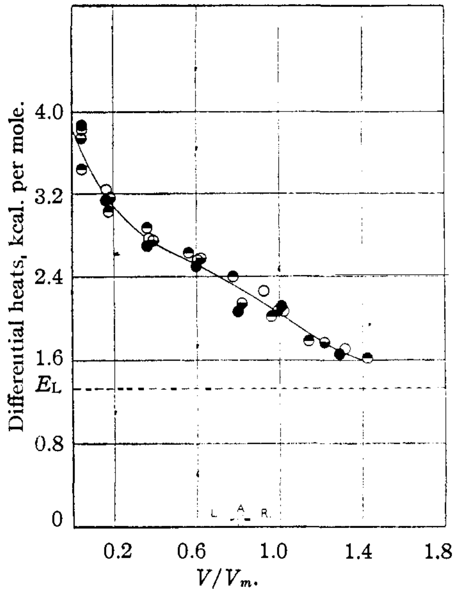

Fig. 6.—Heats of adsorption at −195°; nitrogen on Sterling S and Sterling L: Sterling L, run 27 ◓; run 28 ◒; Sterling S, run 29 ○; run 30 ●.

Discussion

From Figs 3–8 it is apparent, with all the blacks except Graphon, that the differential heats of van der Waals adsorption for the elementary gases studied undergo a large variation as successive fractions of the surface are covered. Moreover, in all cases, the heats approach closely to the value of the heats of liquefaction after the completion of the monolayer as calculated by application of the B.E.T. theory. The latter observa-

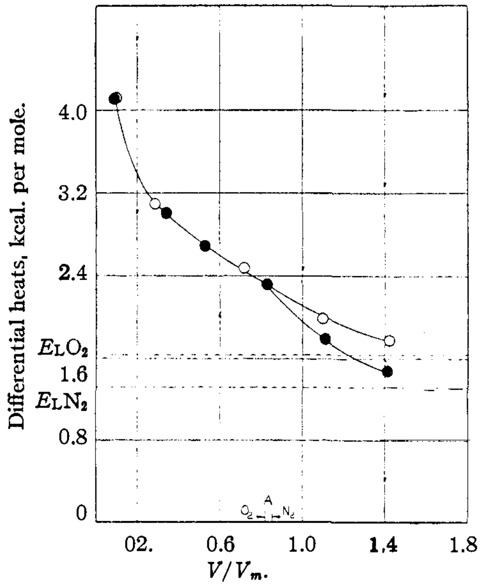

Fig. 7.—Heats of adsorption at −195°; nitrogen and oxygen on Spheron Grade 6: run 14 (nitrogen) ●; run 15 (oxygen) ○.

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[12] Anderson, THIS JOURNAL, 68, 686 (1946).

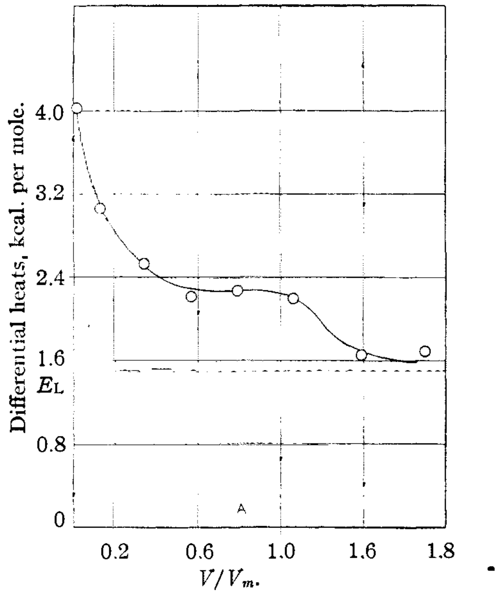

Fig. 8.—Heats of adsorption at −195°; argon on Spheron Grade 6: run 17 O.

tion, while not necessarily giving justification for the assumptions on which the B.E.T. theory is based, does indicate that the theory is useful in estimating the value of v_m, since it is quite reasonable that the energy of binding for the second and successive layers should be of the same magnitude as the heat of liquefaction. In the derivation of theories of physical adsorption,[3] it is frequently assumed as a first approximation that E_1, the heat of adsorption in the first layer, is constant. Although this assumption greatly simplifies the mathematical derivation of any adsorption equation, it is obviously not substantiated in our results, which show variations of the order of 2000 cal. per mole, except for the case of Graphon. However, it should be noted that such a large variation in the value of E_1 would not result in any great change in the value of v_m as calculated by the B.E.T. equation.[13]

It is natural to speculate on the underlying cause for this experimentally observed variation in the heats of adsorption in the first layer. Two possible causes suggest themselves; these are (1) physical heterogeneity of the surface, and (2) lateral interaction between the molecules being adsorbed and the molecules already adsorbed on the surface. It seems to be justifiable to rule out interaction as a sufficient cause in all cases except Graphon. Barrer[14] has made a calculation of the effect of interaction in his investigation of the physical adsorption of nitrogen on graphite, and has come to the conclusion that the dispersion forces due to lateral interaction would account for additional energies of binding of the order of 100 to 200 calories per mole of adsorbate, and moreover that this effect would increase rather than decrease the heat of adsorption as successive fractions of the surface become covered. The observed decrease of 2000 calories within the first layer in the heats for Grade 6 carbon black cannot then be accounted for by interaction.[15] The alternative suggestion that the carbon black surfaces are not homogeneous seems the more tenable way of accounting for the observed decrease in heats.

A comparison of the heat curves which are shown in Figs. 3 and 4 is of considerable interest because we have in Grade 6 Spheron and in "devolatilized" Grade 6 two adsorbents with different chemical state of surface but with practically identical underlying solid material in the carbon black particles. The almost identical behavior in the heats of adsorption curves appears to indicate that it is the state of the underlying solid rather than the presence or absence of a chemisorbed layer, consisting largely of oxygen, which determines the magnitude of the binding energy for the adsorbed molecules of nitrogen. A comparison of the surface activity of the Graphon with Grade 6 Spheron black either before or after "devolatilizing" suggests additional evidence concerning the nature of the heterogeneity in the surfaces of the latter adsorbents. As has already been stated in the description of these blacks, we have in Graphon a much more orderly structure of the carbon atoms in graphitic plates.[4d] It is not unreasonable that the more random arrangement of the underlying solid, in Grade 6 or in the "devolatilized" form, should lead to lack of homogeneity in the surface as compared to Graphon.

In Table III, Column 2, are given the integral heats of adsorption for all the nitrogen adsorbed in the first layer. These values designated as E_1(cal.) were obtained by adding up the total number of calories liberated in the successive

TABLE III

COMPARISON OF HEATS OF ADSORPTION OF NITROGEN IN THE MONOLAYER AT −195° MEASURED CALORIMETRICALLY, E_1(cal.) AND COMPUTED FROM THE B. E. T. EQUATION, E_1(B. E. T.)

Sample	E_1(cal.)[a] kcal. per mole	E_1(B. E. T.) kcal. per mole	E_1(cal.) − E_1(B. E. T.), kcal. per mole
Spheron Grade 6 (MPC)	3180	2180	1000
Spheron Grade 6 "devol."	3100	2250	850
Graphon	3040	2200	840
Sterling S (SRF)	3010	2080	930
Sterling L (HMF)	2880	2140	740

[a] E_1 (calorimetric).

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(13) The form of the equation most frequently used is $p/v(p_0 - p) = 1/v_mC + (C - 1)/v_mC.p/p_0$ in which C is defined as $e^{(E_1 - E_L)/RT}$. Since C is always greater than 100 with carbon blacks, the term $(C - 1)/v_mC$ is always close to $1/v_m$ and the term $1/v_mC$ is close to zero. Hence the slope of the straight line obtained by plotting $p/v(p_0 - p)$ against p/p_0 is approximately equal to the reciprocal of v_m no matter how much C may exceed the minimum value of 100.

(14) Barrer, *Proc. Roy. Soc.* (London), **161A,** 476 (1937).

(15) It is possible that such interaction forces do account for the observed increase in heats for the second half of the monolayer in the case of Graphon.

increments up to the point where $v/v_m = 1$. It was then a simple matter to calculate the integral heats in calories per mole. In Column 3, are presented the E_1(B.E.T.) values computed from the B.E.T. plots of Fig. 2. Although comparison of these values with the calorimetric data is probably not entirely justified on theoretical grounds, such a comparison does reveal that the calorimetrically determined values with nitrogen are some 700–1000 calories greater than those computed from the B.E.T. isotherm. Cassie[16] has suggested that the ratio of the partition function of the nitrogen molecules in the second and higher layers to those in the first layer should be about 50 rather than unity as assumed by B.E.T.[17] As a consequence Cassie points out the heat of adsorption for nitrogen at −195° computed from the B.E.T. theory will be low by about 600 calories. Our calorimetric results appear to give some support to the conclusions of Cassie as is seen in Column 3 of Table III.

While the present experiments have been considered as preliminary and we had not anticipated a close correlation with rubber reinforcing properties, this being the province of the hydrocarbon study to be reported later, the present results nevertheless do permit a degree of generalization on this point. From the data in Table II it is evident that rubber properties of Spheron Grade 6, before and after "devolatilizing" at 927°, are about the same. The present data are in accord with this fact in that they indicate that removal of surface oxides has not altered the high energy sites on the surface of the particle. On the other hand "graphitizing" of this black has markedly lowered its modulus and abrasion resistance properties and the heat of adsorption measurements show clearly that this treatment has effectively decreased the number of high energy sites on the surface. While the present heat measurements do not differentiate between a semi-reinforcing furnace black (Sterling S) and a high modulus furnace black (Sterling L) they do yield values for the initial heats which are intermediate between a fully reinforcing pigment (Spheron Grade 6) and an essentially nonreinforcing pigment (Graphon). It is obvious that a similar comparison of the heats of adsorption of hydrocarbon adsorbates with the rubber reinforcing abilities of the various blacks would have a more direct bearing on the problem of rubber reinforcement. Although we do not wish to anticipate the results of these studies, now in progress, it may be said that the variation in behavior of the hydrocarbons is surprisingly like that of the elementary gases so far as heats of adsorption on the different blacks are concerned.

Summary

1. The differential heats of adsorption of nitrogen and oxygen on a series of carbon blacks of varying rubber reinforcing ability have been determined calorimetrically at −195°.

2. The results are roughly consistent with the predictions of the theory of Brunauer, Emmett and Teller, in that the differential heats of adsorption within the B.E.T. monolayer are greatly in excess of the heats of vaporization, but rapidly approach the heat of vaporization in the second and successive layers observed.

3. However, the magnitude of the integral heats of adsorption for the monolayer is considerably in excess of that calculated from the B.E.T. theory.

4. On the reinforcing blacks, the differential heats undergo large variations as successive fractions of the bare surface are covered. Partial "graphitization" greatly reduces the activity of the more active sites on the surface.

5. Surface activity as revealed by heat measurements appears to parallel the rubber reinforcing properties of the blacks studied.

RECEIVED JULY 2, 1946

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[16] Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

[17] See also Hill, *J. Chem. Phys.*, **14**, 263 (1946).