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SUMMARY

Isotherms and heats of adsorption have been measured for the polar gas sulfur dioxide at 0°C on representative members of a series of carbon blacks graphitized at successively higher temperatures up to 2700°C. In contrast to the behavior of the nonpolar gases nitrogen and argon, which have been studied previously, it is found that removal of oxygen complexes from the carbon surface by high temperature treatment causes the amount of SO₂ adsorption to be sharply reduced and the shape of the isotherm to be altered. On the untreated Spheron carbon black of high surface oxygen content the calorimetrically measured differential heats of adsorption fall steadily with coverage from an initial value of 15 kcal/mole to values which approach the heat of vaporization (5.85 kcal/mole). Treatment at 2700° produces a comparatively uniform, graphite-like surface free from polarizing complexes. On this heat treated material, the differential heats of adsorption start at 6 kcal/mole and then rise with coverage to a maximum of 7.4 kcal/mole; this rise with coverage is attributed to lateral van der Waals forces between the adsorbed molecules. As might be expected, the heat values for Spheron (1000°) vary in a manner which is intermediate between the two extremes represented by Spheron and Spheron (2700°). From the data on the highly graphitized carbon, Spheron (2700°), it is concluded that (1) there is no sharp separation, as in the case of argon, between first and second layer formation of SO₂ at 0°, and (2) lateral dipole repulsions between adsorbed polar SO₂ molecules are small in comparison with van der Waals attractive forces.

INTRODUCTION

Wide use is now being made of the physical adsorption of nitrogen at liquid air temperatures for the determination of the surface areas of finely divided nonporous solids. The volume of nitrogen required to form a single layer of adsorbed molecules may be deduced from the empirical point 'B' in the adsorption isotherm or, in the case of non-uniform surfaces only, from the equation of Brunauer, Emmett and Teller.¹ The success of this method lies, to a considerable degree, in its equal applicability to polar and nonpolar solids, since the

form of the isotherm, in the case of nitrogen, is relatively independent of the chemical state of the adsorbing surface. This point may be illustrated by the almost identical nature of the isotherms and of the heats of adsorption for nitrogen on a sample of carbon black (Spheron 6) having about 5% of oxygen incorporated in the surface layers and on the "devolatilized" carbon produced by heating the Spheron to 927°C.² At this temperature some 90% of the oxygen was evolved, the physical structure of the carbon particles remaining essentially unchanged. The surface of the original, oxygen containing, Spheron would be expected to be polar in nature. In general, the applicability of the nitrogen adsorption method to determining the surface areas of both polar and nonpolar substances has been confirmed by measurements of the entropy of adsorption^{3,4} which indicate monolayer coverages in accord with those obtained from the isotherm.

While the physical adsorption of nitrogen appears generally to be independent of the chemical nature of the adsorbent surface, it should be noted that this is not universally true. Stone and Tiley⁵ have demonstrated that the physical adsorption of gases on metallic oxides may be markedly influenced by the presence of pre-adsorbed carbon monoxide. This modification of a nitrogen isotherm appears to be a specific effect, being dependent not only upon the molecular species preadsorbed, but also upon its configuration at the surface.⁶ From a practical point of view, these results illustrate the importance of adopting an adequate outgassing procedure before undertaking surface area measurements.

When considering the physical adsorption of polar molecules, in contrast to nitrogen or the inert gases, we might expect rather widely different adsorption effects in dealing with surfaces of varying chemical composition and consequent varying degrees of polarity. This is indeed true, as shown by Anderson and Emmett⁷ for adsorption of water and ammonia on the above mentioned pair of carbons. When the removal of the oxygen is virtually complete, as with the pigment Graphon produced by heat treatment of carbon blacks to temperatures approaching 3000°C, the adsorption of water vapor is greatly reduced and the isotherm shifts to an extreme Type III.⁸ Thus it would be possible to use water vapor adsorption to estimate the degree of polarity of any given carbon surface. This method, however, is experimentally inconvenient and is further complicated by the slow chemical reaction of water with a carbon surface.⁸ In the present paper it is demonstrated that sulfur dioxide may also be utilized in studying the polarity of adsorbent surfaces. It meets the requirements of being a suitable polar adsorbate (dipole moment = 1.60 Debye Units), while being convenient for use at 0°C.

A sharp change is found in comparing the sulfur dioxide isotherms of an oxygen containing surface with one from which the oxygen has been removed.

The effect of high temperature treatment of carbon blacks upon their adsorptive properties is a subject currently of general interest. A series of carbon black samples prepared by treating Spheron at successively higher temperatures up to 2700°C has been described by Schaeffer, Smith and Polley,⁹ who have shown by x-ray and electron microscope techniques that there is a gradual transition from a heterogeneous to a more homogeneous surface. This transition is a result of progressive graphitization of the carbon particles and an increase of three-dimensional order within the crystallites. The adsorption of the nonpolar gas argon on this series of carbon blacks has been studied^{10,11} and the heats of adsorption are reported in Technical Report No. 3. With increasing temperature of graphitization, the isotherms change progressively from normal Type II to isotherms of stepwise character. Such stepwise isotherms have been theoretically predicted for adsorption on a homogeneous surface.^{12,13} The amount of adsorption at a given relative pressure is, however, essentially unchanged, as would be expected for a nonpolar molecule like argon or nitrogen. Heat measurements for argon adsorption demonstrate even more clearly the increasing homogeneity of the carbon surface with increasing temperature of graphitization. With the original Spheron sample the differential heat of adsorption shows a progressive decrease as the surface is covered, this being characteristic of heterogeneous surfaces. Conversely, on the sample graphitized at 2700°, the surface is much more homogeneous in adsorption potential with the result that the van der Waals attraction between adjacent adsorbed molecules is clearly demonstrated by a steady rise in the differential heat as the first monolayer is filled. At the completion of a monolayer the heat drops sharply as second layer formation commences.

The experimental evidence indicates that in Spheron (2700°) we have a highly reproducible, chemically pure carbon adsorbent which has an essentially homogeneous surface of comparatively high surface area. Adsorption data on such a surface are undoubtedly more amenable to theoretical treatment than data obtained on surfaces which are chemically and geometrically more complex. Several theoretical calculations of the heat of adsorption of argon on uniform surfaces have been made⁽¹⁴⁻¹⁶⁾ and compared with data obtained experimentally. However, attempts at similar calculations for polar molecules have been subject to an uncertainty as regards the orientation of the adsorbed molecules and thus of the coulombic forces between them.

Calculations for the adsorption of SO_2 on conductors by Roberts¹⁷ and on ionic solids by Crawford and Tompkins¹⁸ are based on the assumption that the dipoles of the adsorbed molecules are oriented in a square array. Using this model, it is suggested that van der Waals attraction and coulombic repulsion between adsorbate molecules are of the same order of magnitude, preventing the heat of adsorption from varying greatly with increasing surface coverage.

By experimentally measuring the heat of adsorption of a polar gas such as sulfur dioxide as a function of surface coverage on the uniform Spheron (2700°), we hoped to be able to draw inferences about the relative contributions of van der Waals attraction and dipole repulsion to the lateral interaction forces between adjacent molecules. The results suggest that dipole repulsion between adjacent molecules is of little significance compared with van der Waals attraction.

EXPERIMENTAL

Materials.

Sulfur dioxide was obtained from the Matheson Company; the purity was stated as 99.7%. After transfer to the adsorption train it was subjected to bulb to bulb distillation under vacuum and the middle portion of the distillate was finally used. Oxygen was prepared from analytical grade potassium permanganate and dried over phosphorus pentoxide. The series of heat treated carbon blacks described by Schaeffer, Polley and Smith⁹ was used, the samples studied being Spheron 6, Spheron (1000°), Spheron (1500°), and Spheron (2700°).^{*} The specific surface areas of these four carbons, as determined by Polley et al¹⁰ by nitrogen adsorption, are 114, 91.1, 88.0, and 84.1 sq.m/g. respectively. In the present investigation, we shall be especially interested in the effect of the chemical composition of the samples on their $\neq$ adsorptive characteristics. Analysis of the carbon blacks is given in Table 1. Unfortunately, the oxygen data, with which we

* The temperature of heat treatment is indicated: Spheron (1500°) indicates a sample of Spheron treated for two hours at 1500°C.

$\neq$ Phillips Petroleum Co. data.

Table 1.

	<u>% Loss Drying¹</u>	<u>% Hydrogen</u>	<u>% Carbon</u>	<u>% Ash</u>	<u>% Sulphur</u>	<u>% Oxygen²</u>
Spheron 6	1.83 1.71	0.60 0.59	95.17 95.11	0.05 0.11	0.25 0.25	3.93 3.94
Spheron (1000°)	0.08 0.06	0.15 0.13	99.20 99.22	0.11 0.11	0.25 0.26	0.29 0.28
Spheron (1500°)	0.00 0.00	0.02 0.02	99.70 99.73	0.08 0.07	0.09 0.09	0.11 0.09
Spheron (2700°)	0.01 0.00	0.00(5) 0.00(2)	99.87 99.91	0.06 0.03	0.00(2) 0.00(3)	0.06(3) 0.05(5)

1. Drying condition: 1 hour in stream of dry nitrogen at 150°C.
2. By difference.

are especially concerned, are determined by difference only. However, the results of Table 1 for both hydrogen and oxygen content of the original Spheron are in qualitative agreement with the data of Emmett and Anderson.⁷ The results illustrate well the high purity of Spheron (2700°) and the negligible sulfur content is especially reassuring in view of the investigations of Smith, Pierce and Joel; which showed an appreciable sulfur content in a previously prepared sample of Graphon.¹⁹

A single adsorption isotherm was made on a sample of graphite obtained from the same batch as used by Pierce et al.,⁸ which was reported to have an ash content of below 0.001% and to be essentially free of oxygen complex. Its surface area (nitrogen adsorption) was 4 sq.m/g.

Apparatus and Procedure.

The apparatus used in measuring the isotherms and in the determination of the heats of adsorption was identical with that described in Technical Report No. 3. All adsorptions were carried out at 0°C, crushed ice being used as a constant temperature medium. The vapor pressure (P_0) of SO_2 at 0°C is 116.5 cm.²⁰ After standing overnight, the thermocouple temperature was constant to better than $\pm 0.002^\circ\text{C}$, making for ideal calorimetric conditions.

Heat measurements were made using the calorimeter both isothermally and in a manner which was essentially adiabatic. The isothermal method, using helium in the outer vessel of the calorimeter, has been described in Technical Report No. 1. In the "adiabatic" method the outer vessel was highly evacuated and cooling was quite slow. From the cooling curve the Newton Cooling Coefficient was calculated and the adiabatic time-temperature curve was reconstructed. Within two or three minutes after the heat was released, the adiabatic curve reached a constant value. This method yielded rather more consistent and reliable results, but because of the time-consuming calculations involved, its use was restricted to the measurements on Spheron (2700°), the sample of greatest fundamental interest.

Consideration was given to correcting the measured heats for the heat of compression of the gas within the calorimeter, as given by the equations of Kington and Aston.²¹ In each case the correction was less than 1%, which is well within the estimated experimental accuracy ($\pm 3\%$). Although this correction was not made it is justifiable to regard the heats plotted in Figures 4 - 7 as isosteric heats which are designated as q_{st} .

Before each run the sample was thoroughly evacuated overnight at 200-250°C. The SO_2 was measured in a gas buret and admitted to the adsorbent. In the case of the heat treated carbons the adsorption was rapid and equilibrium was attained in a few minutes; there was no desorption hysteresis. With the original Spheron, a continued slow uptake was observed after the initial rapid adsorption and it was necessary to allow more than an hour for equilibrium. This continuing slow uptake was too slight to introduce appreciable error into the heat measurements.

Dead space calibrations were carried out with helium, and consideration was given to correcting for the non-ideality of SO_2 in respect of (1) the residual unadsorbed gas, (2) the volume measured in the buret. In estimating these corrections the virial equation was used, a mean value of -370 being taken for the second virial coefficient of SO_2 at 0°C. Both corrections were less than 1% in the worst case and usually far smaller; in general these were not made.

RESULTS

Isotherms.

Figure 1 shows the adsorption isotherms of SO_2 at 0°C on the four carbon blacks. The marked drop in adsorptive capacity of Spheron (1000°) compared with the original Spheron parallels the loss of oxygen (Table 1). The question arises

as to whether storage of the samples in air at room temperature causes the formation of a surface layer of oxide not removed by our standard procedure of evacuation at 200-250°C. If this were so, adsorption of SO_2 on all of the graphitized carbons presumably would be higher than for a pure carbon surface. To demonstrate that no oxygen not removable by evacuation at 250°C was adsorbed from the air, Spheron (2700°) was placed in a platinum bucket contained in a quartz tube and evacuated for 24 hours at 950-1000°C. After cooling in vacuum, the SO_2 isotherm was repeated in situ. Figure 2 shows that the isotherm was identical with that for Spheron (2700°) which had been evacuated at 200-250°C. As a further test, a sample of the original Spheron was also evacuated for 24 hours at 1000°C, cooled in vacuum and an SO_2 isotherm was run. This isotherm was almost identical to that for Spheron (1000°) - see Figure 2. This agreement must be considered excellent if we bear in mind that our experimental conditions for producing a sample by evacuation at 1000°C were quite different from those obtaining in production of Spheron (1000°) in the Cabot Laboratories.⁹ We conclude from these two experiments that our standard outgassing procedure is adequate to remove any oxygen taken up from the atmosphere during transfer and storage.

Spheron itself is undoubtedly highly complex, the presence of both hydrogen and oxygen giving rise to the possibility of many different surface complexes. Such a surface is perhaps of little fundamental interest and so an attempt was made to produce artificially a somewhat simpler polar surface by high temperature treatment of the devolatilized carbon black with oxygen alone. Spheron (1000°) was heated to 600°C for two hours in contact with oxygen and then allowed to cool (still in oxygen) to room temperature. The volume of oxygen taken up was comparatively small, but no reliable estimate may be given as the residual gas was not analyzed for CO and CO_2 . A sulfur dioxide isotherm was then measured (Figure 2). It is at once apparent that the adsorption of SO_2 by a devolatilized carbon black is enhanced by pre-treatment with oxygen.

Figure 3 shows a single isotherm measured for the adsorption of SO_2 on graphite. Its shape is essentially that of the isotherm on Spheron (2700°) and if the volume axis is multiplied by the ratio of the surface areas of the samples (a factor of 21) it is seen that the isotherms may be almost exactly superimposed. This experiment indicates that the graphite and the Spheron (2700°) are similar in that both have surfaces which are comparatively uniform with respect to adsorption potential.

Heat Measurements.

Differential heats of adsorption of SO_2 as a function of surface coverage were measured for Spheron, Spheron (1000°), and Spheron (2700°). These are shown in Figures 4, 5 and 6. The difference in the shape of the heat curves for the three samples is most striking.

In Figure 7 the heat of adsorption of SO_2 at low surface coverages on Spheron (1000°) and oxygen treated Spheron (1000°) are compared. As might have been expected from Figures 4-6, the heat of adsorption is observed to be somewhat higher on the oxygenated surface.

Entropy of Adsorption.

Recently, Hill, Emmett and Joyner³ have given a theoretical treatment of entropies of adsorption and have indicated how monolayer coverages may be deduced from integral entropy values. The integral entropy of adsorption ($S_s - S_g$) may be calculated from a pair of isotherms at different temperatures by the equation²²

$$\left(\frac{\partial \ln P}{\partial T} \right)_\phi = -(S_s - S_g)/RT \quad (1)$$

Here, ϕ is the spreading pressure, given by the Gibbs equation

$$\phi = RT \int_0^\Gamma \Gamma \, d \ln P (T \text{ const.}) \quad (2)$$

where Γ = surface concentration

$\Gamma = N/A$ (N = number of mols. adsorbed on area A .)

Such a procedure has been used in entropy calculations for the adsorption of nitrogen³ and ethyl chloride²³ on Graphon.

Jura and Hill²⁴ pointed out that the integral entropy of adsorption could be computed more accurately using a calorimetric heat of immersion or heat of adsorption and a single isotherm. To date, such calculations have been made by Zettlemoyer et al²⁵ measuring heats of immersion and Drain and Morrison²⁶ measuring heats of adsorption.

In the present work, the integral entropy of adsorption of SO_2 on Spheron (2700°) was calculated using the equation

$$(S_s - S_g) = -Q/T - R \left[\int_0^V \ln P \, dV - V \ln P \right] \quad (3)$$

where Q is the integral calorimetric heat.

(This equation is eq. 6 of Drain and Morrison, ignoring the small correction factor for gaseous imperfection which would be within our calorimetric experimental error.)

Substituting the heat of vaporization of SO_2 at 0°C , $E_L = -5850 \text{ cal}$,²⁷ in the Gibbs Helmholtz equation, we may calculate the entropy of vaporization (ΔS_L) at 0°C .

$$\begin{aligned}\Delta S_L &= \frac{E_L}{T} - R \ln P_0/P \\ &= -30.87 + R \ln P\end{aligned}\quad (4)$$

The net integral entropy of adsorption is then given by

$$(S_S - S_L) = (S_S - S_g) - \Delta S_L \quad (5)$$

Large scale graphs of $\log P$ against V for adsorption of SO_2 at 0°C on Spheron (2700°) were numerically integrated and the net integral entropy of adsorption ($S_S - S_L$), calculated according to equations 3-5, is shown in Figure 8. The SO_2 isotherm is particularly well suited to this type of calculation since there is relatively little adsorption at low pressure and, consequently, it is not necessary to take readings in the McLeod pressure range as for nitrogen adsorption. In making the calculation, a linear isotherm $V = kp$ was assumed below a coverage of 0.5 cc/g . This approximation is justifiable since $\int_0^{0.5} \ln P \, dV = -0.23$, which is small compared with the total integral $\int_0^{16.5} \ln P \, dV = 44.23$. In general, the calculation of integral entropies and of spreading pressures for adsorbates which show an isotherm convex to the pressure axis does not require adsorption data at very low pressures.

Figure 8 shows also the net differential entropies of adsorption ($S_S - S_L$) calculated from the differential calorimetric heats. No attempt was made to calculate entropy values for adsorption on Spheron as the surface is not of such fundamental interest as is that of the graphitized material and the low pressure data necessary with Type II isotherms were not available.

Spreading Pressure

Harkins, Jura et al²⁸ have calculated the decrease in surface free energy during adsorption processes. This decrease is, by definition, equal to the spreading pressure of the adsorbed film given by the Gibbs equation (2). Calculation of the spreading pressure ϕ as a function of area per adsorbed molecule σ has proved fruitful in demonstrating phase transitions both in monolayers spread on liquid surfaces and in gases adsorbed on solids. From the magnitude of the spreading pressure, information about the physical nature of the adsorbed monolayer may be deduced.

The spreading pressure exerted by SO_2 adsorbed on Spheron (2700°) was calculated according to equation (2) and is plotted in Figure 9 as a function of σ .

DISCUSSION

A comparison of the isotherms shown in Figure 1 with a similar set of isotherms for argon on the same series of carbon adsorbents¹¹ reveals a marked difference in the behavior of the polar SO_2 and the nonpolar argon adsorbates. While heat treatment of the carbon black has little effect on argon adsorption, there is a strong effect on SO_2 adsorption, the amount of SO_2 adsorbed at a given relative pressure being greatly reduced. The heat of adsorption on untreated Spheron is appreciably higher than on the heat treated carbons. These observations illustrate the influence of a polarizing surface in enhancing the adsorption of a polar molecule. The sustained high heat values for Spheron indicate that the influence of the polarizing surface extends into second layer adsorption ($V_m = 16.1 \text{ cc/g.}$ based upon the cross sectional area $\sigma_{\text{SO}_2} = 19.4 \text{ \AA}^2$ from liquid density measurements.)

Consideration was given to the possibility that the high heat values on untreated Spheron were due to chemisorption of SO_2 by surface complexes rather than to electrostatic orientation effects. Although it cannot be stated for certain that a chemical bond is not formed, it has been shown that the surface of Spheron is acidic in nature²⁹ and so any reaction analogous to salt formation appears to be ruled out for SO_2 . Moreover, the isotherms of Crawford and Tompkins¹⁸ for adsorption of SO_2 on polar crystals of BaF_2 and CaF_2 resemble those on Spheron in being of Type II, monolayer formation occurring at approximately the same relative pressure (about 0.1).

Heat treatment of Spheron at 1000°C is known to remove most of the oxygen from the carbon, while x-ray studies show that little graphitization occurs at this temperature.⁹ Thus Spheron (1000°) possesses a nonpolarizing surface with sites of varying adsorption potential. Such a picture is in accordance with the heat coverage curve for SO_2 on Spheron (1000°). The high initial heats are indicative of a heterogeneous surface, but, after a sharp drop, the heat reaches a value which is much lower than for Spheron. In the same manner as for argon adsorption,¹¹ the fall in heat with coverage due to surface heterogeneity offsets the tendency to show a rise due to van der Waals attraction between adjacent adsorbed molecules. After graphitization at 2700°C , the surface is far more uniform and the effect of lateral interactions between adjacent adsorbed molecules manifests itself as an increase in heat of adsorption with coverage. Similar results were obtained for argon¹¹ and ethyl chloride.²³

The increasing uniformity of the carbon surface on graphitization is illustrated also by the changing shape of the SO_2 isotherms for Spheron (1000°), Spheron (1500°), and Spheron (2700°). After heat treatment to 2700°, the SO_2 isotherm is actually convex to the pressure axis at low pressures. This result will be discussed in relation to the behavior of other polar adsorbates on the same uniform surface in a future paper.

Adsorption of sulfur dioxide by nonporous carbons has not been investigated previously. With porous charcoals, Polanyi and Welke³⁰ reported a two-dimensional condensation of SO_2 on the surface at a few percent coverage. Calorimetric measurements of adsorption on charcoal by Magnus and co-workers³¹ provided no evidence for such a surface condensation. In the present work with nonporous carbon Figure 9 indicates that no first order phase transitions occur in the pressure range with which we are dealing. Moreover, the value of $\phi\sigma$ at low coverages ($\phi\sigma = 360 \times 10^{-16}$ ergs/molecule) is almost identical with that for a perfect two-dimensional gas, indicating that the adsorbed SO_2 exists as a gaseous expanded film and that condensation has not occurred at pressures lower than those measured by our technique. We conclude that two-dimensional condensation of SO_2 does not occur on a uniform, nonporous carbon surface at 0°C.

In Table II we have summarized the calorimetric data for the adsorption of sulfur dioxide at 0°C and argon at -195°C on Spheron (2700°). The first point of interest is that the initial heat of adsorption of SO_2 on this uniform surface is

Table II.

Gas.	E_L , Kcal	$q_{st}(\text{initial})$, Kcal	$q_{st}(\text{max})$, Kcal	$\frac{q_m - q_i}{\text{Kcal}}$	$\frac{q_m - E_L}{E_L}$
Argon	1.57	2.7	3.2	0.5	1.04
Sulfur Dioxide	5.85	6.0	7.4	1.4	0.26

comparable with the heat of vaporization E_L , whereas for argon, $q(\text{initial}) = 1.7 E_L$. Although the net heat of adsorption of SO_2 is initially almost zero, the entropy of the molecules in the adsorbed film at low coverages is appreciably higher than in the liquid (Figure 8); thus the free energy of adsorption exceeds that of liquefaction. Such a result illustrates the importance of considering free energy changes in adsorption processes and suggests that even negative net heats of adsorption might possibly occur in certain instances.

The SO_2 -Graphon system is probably the first recorded example in which the heat of adsorption is initially almost zero and increases with increasing surface coverage.

Several theoretical calculations of the heat of adsorption of gases on a uniform carbon surface (graphite) have been made, but uncertainty arises as to whether the adsorbent should be treated as a metallic conductor or as a covalent solid.³² Crowell and Young¹⁶ recently have calculated the heat of adsorption of argon on a bare graphite surface, but reliable calculations for polar molecules are believed not to be feasible at present.

The maximum value of the heat of adsorption of SO_2 on Spheron (2700°) occurs at a surface coverage of about 12 cc/g. This is less than the monolayer coverage of 16 cc/g., based upon the value of σ_{SO_2} for close packing. No distinct point 'B' is apparent in the isotherm suggesting that there is no clear-cut separation between first and second layer formation. An approximate value of point 'B' of 10-13 cc/g. agrees with the maximum in the heat curve. Hill, Emmett and Joyner³ have suggested that the criterion of monolayer completion is the point of intersection of the differential and integral entropy curves. Figure 8 shows that in the present work these do not intersect and suggests that second layer formation begins around 12 cc/g., before a monolayer is completed. The heat curve beyond this point is probably composite, representing both first and second layer formation. It therefore falls more gradually than does the corresponding graph for argon adsorption, where the heat drops sharply at the monolayer value and there is a clear distinction between first and second layers.

This difference in behavior of argon and sulfur dioxide is associated with the difference in the net heat of adsorption at the maximum ($q_m - E_L$) compared with the heat of liquefaction E_L . (See Table II.) The much lower value of the relative net heat at the maximum ($\frac{q_m - E_L}{E_L}$) for SO_2 compared with argon causes a smearing out of any sharp distinction between first and second layer formation. Of course the higher thermal energy at 0°C ($kT = 550$ cal) compared with -195°C ($kT = 160$ cal) would make for greater disorder of the adsorbate, and this too would lead to a greater blurring of first and second layer adsorption in the case of the SO_2 .

When considering lateral interactions between adsorbed polar molecules, allowance has to be made for coulombic repulsion between dipoles as well as for van der Waals attraction. Langmuir³³ first pointed out that dipoles

arranged in a parallel array exert a mutually depolarizing effect on one another, giving rise to a decrease in dipole moment as the surface becomes covered and thus reducing intermolecular coulombic repulsion. Various theoretical estimates^{17,34} for sulfur dioxide and also for ammonia have suggested that the dipole repulsion between adsorbed molecules is of the same order of magnitude as the van der Waals attractive interaction. For a uniform surface, this results in a heat of adsorption which varies but slightly with coverage. In the present study, the heat of adsorption of SO_2 on Spheron (2700°) rises steadily with coverage up to 12 cc/g. This observation leads to the conclusion that either the depolarizing effect of the dipoles upon each other is greater than formerly estimated, or else the dipoles (and thus the SO_2 molecules) are randomly oriented at the surface.

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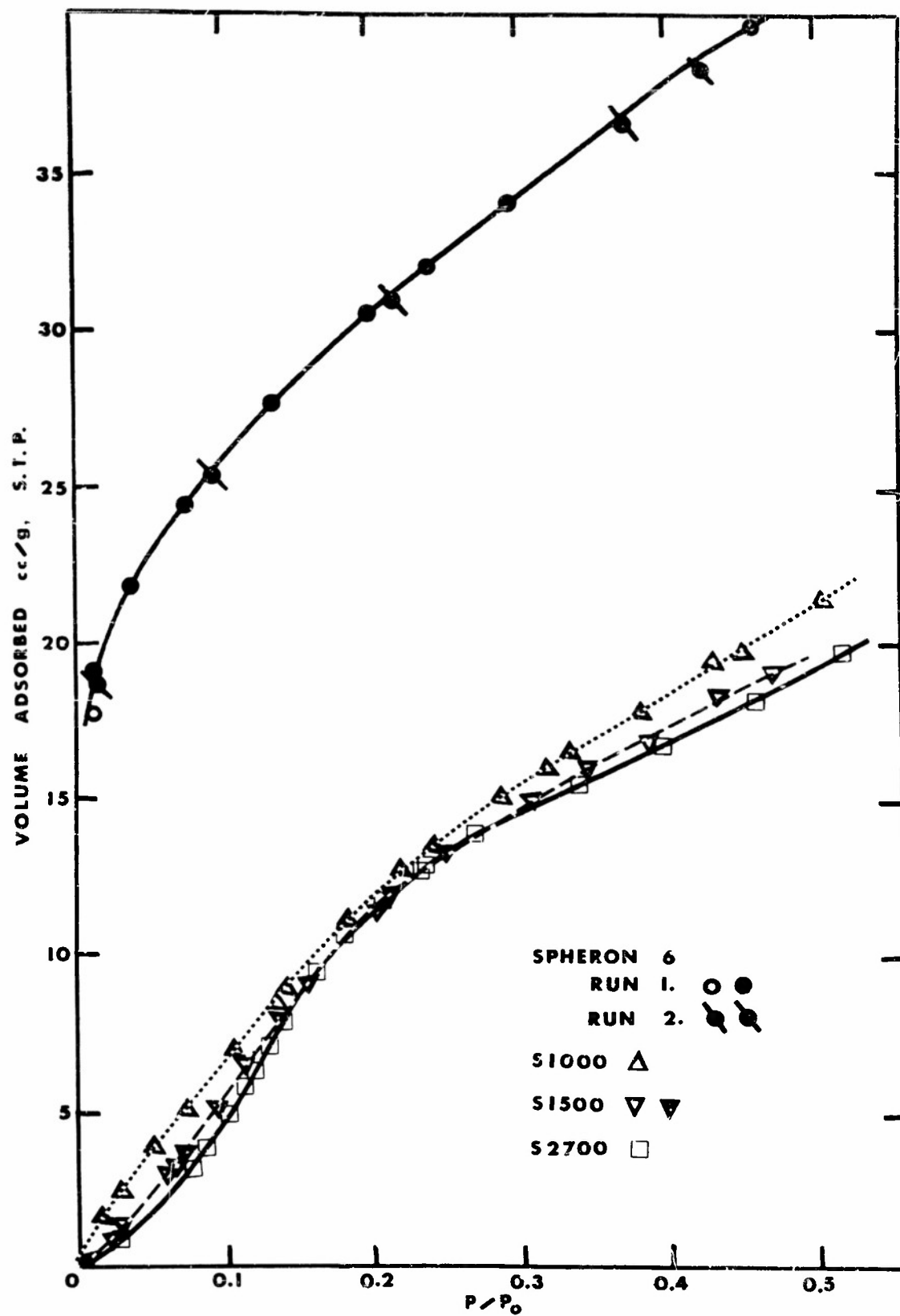


FIGURE 1
ISOTHERMS, SO_2 ON CARBON BLACKS AT 0°C

ADSORPTION POINTS OPEN
DESORPTION POINTS BLACKENED

