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HEATS OF ADSORPTION OF POLAR MOLECULES ON CARBON SURFACES

II. *Ammonia and Methylamine*

R. A. Beebe and R. M. Dell

Office of Naval Research

Technical Report

Number 5

August 1954

Research Contract

N8-onr-66902

Project Number

NR-358-151

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Department of Chemistry

Amherst College

Amherst, Massachusetts

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SUMMARY

Isotherms in the temperature range from -78° to -22°C have been measured for ammonia on representative members of a series of carbon blacks graphitized at successively higher temperatures up to 2700° ; and heats of adsorption for ammonia on these blacks have been calorimetrically determined at -78° . A limited number of experiments have been done with methylamine.

In comparison with argon and sulfur dioxide previously studied, the ammonia presents the additional possibility of hydrogen bond formation. This may occur between the ammonia molecules and oxygen complexes on the untreated carbon surface resulting in the observed high adsorption at low relative pressures and high heat of adsorption. With the heat-treated, highly graphitized materials however, there is relatively little attraction of the carbon surface for the ammonia molecules with the result that the isotherm is convex to the pressure axis up to about 0.5 relative pressure, going through a point of inflection to become concave to the pressure axis. The heats of adsorption of ammonia on the graphitized black, Spheron (2700°), are particularly interesting in that they are (1) virtually constant at all coverages and (2) approximately equal to the heat of vaporization of ammonia. The significance of the heats in relation to the isotherms is discussed and a model for the adsorbed film is presented in which the ammonia adsorption occurs in patches one molecule thick. It is suggested that adjacent adsorbate molecules are held together within these patches by forces of lateral interaction which is largely due to hydrogen bond formation.

There is an apparent anomaly in the ammonia isotherms on Spheron (2700°) in that adsorption increases with temperature at a given relative pressure. This observation is discussed in relation to the heats of adsorption.

INTRODUCTION

Recent investigations in this laboratory have been concerned with the adsorption of gases on carbon black surfaces. In particular we have studied a series of blacks which have been graphitized at successively higher temperatures up to 2700° . The adsorbates used in these studies were argon,¹ a non-polar gas, and sulfur dioxide,² a typical polar adsorbate. The following two observations, which have a bearing on the present work, have come out of the research mentioned above: (1) the adsorption of sulfur dioxide, unlike that of argon, is markedly sensitive to presence of oxygen complexes on the carbon surface, (2) on the most homogeneous,

highly graphitized carbon, there is strong positive lateral attraction between the adsorbed molecules whether they be argon or sulfur dioxide.

Following the studies with argon and sulfur dioxide, it is a natural step to extend the experiments to include adsorbates like water and ammonia which are capable of hydrogen bonding. Such hydrogen bonding may be expected to occur between adjacent adsorbed molecules or between adsorbed molecules and the surface if the latter contains oxygen complexes. Of the adsorbates capable of hydrogen bond formation, methanol³ and water^{4, 5} have been studied by adsorption calorimetry. The net differential heat of adsorption of methanol on Graphon has a small positive value which changes only slightly with coverage. Conversely, negative net heats of adsorption have been found for water on Graphon which is essentially the same as Spheron (2700°). Our calorimetric technique is not adaptable to the water-carbon system because in this case so little adsorption occurs before a high relative pressure has been reached. The present work has therefore been confined to ammonia and methylamine which can be handled conveniently. Particularly in the case of the system ammonia-Spheron (2700°), in support of a possible model of the adsorbed film, the heat-coverage data has provided experimental evidence which is considerably more convincing than that provided by the isotherms alone.

Evidence concerning the degree of hydrogen bonding in water adsorbed on porous silica gel and on alumina has been obtained by Freymann and Freymann⁶ by means of microwave absorption. Milligan and Whitehurst⁷ have measured the diamagnetic susceptibility of vapors adsorbed on silica gel. These authors conclude that, for water and propyl alcohol, hydrogen bonds are not formed between adsorbate molecules at less than monolayer coverage, but that in subsequent layers hydrogen bonding does occur.

Interpretation of data obtained by physical techniques such as microwave absorption and magnetic susceptibility, when applied to adsorption on a porous solid, is complicated by uncertainty regarding the surface area of the adsorbent and by the possibility of capillary condensation. Thus it has seemed to us to be appropriate to study the nonporous carbon blacks. In particular the Spheron (2700°) black, in addition to being nonporous, represents a nonpolarizing, physically homogeneous surface. On this adsorbent, ammonia appears to be adsorbed in patches one molecule thick with hydrogen bonding between adjacent ammonia molecules in the patches.

There are on record few theoretical treatments of the adsorption of polar molecules or of molecules capable of hydrogen bonding. Calculations of the heat of adsorption of ammonia on conductors by Roberts,⁸ on nonconductors by Miller⁹ and on ionic crystals by Crawford and Tompkins¹⁰ have not taken consideration of hydrogen bond formation between adsorbed ammonia molecules. It is our belief that such a theoretical approach as that made by the above investigators cannot at present be very fruitful when applied to the ammonia-Spheron systems because of the absence of any definite information concerning the orientations of the laterally hydrogen bonded ammonia molecules on the surface.

EXPERIMENTAL

Materials

Ammonia of stated purity 99.9% was supplied by the Matheson Company. The gas was admitted to an evacuated system, liquefied at -78° , dried over metallic sodium and subjected to two bulb to bulb distillations. The middle fraction of the distillate was collected and stored.

Methylamine was prepared by treatment of methylamine hydrochloride with calcium hydroxide. Both solid reagents were first thoroughly outgassed in a vacuum system, the hydrochloride being kept at -78° together with a little frozen water. On subsequent mixing of the reactants with gentle warming, the methylamine was evolved and dried by passing over solid potassium hydroxide. The gas was condensed and redistilled several times over further potassium hydroxide to insure drying.

Helium of 99.9% purity was also obtained from the Matheson Company. Three samples of carbon black were employed: the parent material Spheron 6, together with heat treated samples Spheron (1000 $^{\circ}$) and Spheron (2700 $^{\circ}$).^{*} Treatment at 1000 $^{\circ}$ removes most of the oxygen which is chemisorbed on the surface of Spheron, while heating to 2700 $^{\circ}$ results in a graphitization process producing a highly uniform, graphite-like surface. The surface areas of these carbons, as measured by nitrogen adsorption, are Spheron 114 sq. m. per g., Spheron (1000 $^{\circ}$) 91.1 sq. m. per g., Spheron (2700 $^{\circ}$) 84.1 sq. m. per g.¹¹ Analytical data are given in Technical

* The temperature of heat treatment is indicated: Spheron (1000 $^{\circ}$) indicates a sample of Spheron treated for two hours at 1000 $^{\circ}$ C. The Spheron (2700 $^{\circ}$) is essentially the same as Graphon which has been previously studied [J. Am. Chem. Soc., 69, 95 (1947)].

Report No. 4 and the structure of graphitized carbon black is discussed fully in the paper of Schaeffer, Smith and Polley.¹²

Apparatus and Procedure

Adsorption isotherms of ammonia on carbon black were determined at various temperatures between -78° and 0° . For measurements at 0° an ice-water constant temperature bath was employed, while for -78° dry ice was used. Intermediate temperatures were obtained with baths of melting organic substances, i. e. tetrachloroethylene (-22°), ethylene dichloride (-36°) and chlorobenzene (-46°). These were each redistilled before use. Two ammonia vapor pressure thermometers were constructed covering the range 0-1 atmosphere (below -33°) and 1-2 atmospheres (-33° to -18°). As each adsorption point on an isotherm was measured, the value of P_0 recorded on the vapor pressure thermometer was observed and used to compute P/P_0 . The temperature of the bath did not fluctuate by more than $\pm 0.15^{\circ}$ during any run, as shown below.

<u>Bath</u>	<u>Measured P_0, cm.</u>	<u>Temperature*</u>	<u>M. Pt.**</u>
$\text{CCl}_2=\text{CCl}_2$	129.2 - 129.6	$-22.2 \pm 0.05^{\circ}$	-22.35°
$\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$	64.8 - 65.6	$-36.3 \pm 0.1^{\circ}$	-35.3°
$\text{C}_6\text{H}_5\text{Cl}$	39.2 - 39.4	$-45.7 \pm 0.0^{\circ}$	-45.1°
Dry Ice	4.05 - 4.15	$-78.8 \pm 0.15^{\circ}$	-78.5°

Except for the calorimeter, an all-glass vacuum system of the conventional type was employed. Increments of gas were measured in a water jacketed buret and the volume of residual unadsorbed gas calculated from deadspace calibrations made with helium. Consideration was given to correcting for the nonideality of ammonia with respect to (1) the residual unadsorbed gas (2) the volume measured in the buret. In estimating these corrections, the virial equation was used, the second virial coefficient of ammonia being given by the data of Keyes.¹³ The correction to be applied to the unadsorbed gas varied from 0.1 to 0.4% and the correction to the gas measured in the buret was approximately 0.3%. These corrections were considered to be within experimental error and therefore were not made.

Adsorption of ammonia on Spheron (2700 $^{\circ}$) was rapid and equilibrium was established almost at once; repeated runs on this adsorbent showed the measurement to

* Based on vapor pressure data from International Critical Tables.

** The melting points were taken from the Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., (1953).

be highly reproducible. In the case of the original Spheron, there was a rapid initial adsorption followed by a slow uptake which continued for several hours. After the first few minutes the rate was insufficient to introduce detectable error into the heat measurements. Similar results were found for the rate of adsorption of sulfur dioxide on these two carbons.² Adsorption of methylamine on Spheron (2700°) was not so rapid as that of ammonia and complete equilibrium was not attained in the first few minutes.

Calorimetric measurements were made for adsorption of ammonia at -78° on all three carbon blacks and for methylamine at 0° on Spheron (2700°). In addition, heats were measured at 0° for adsorption of a few increments of ammonia on Spheron (2700°). The latter measurements could not be extended beyond a low surface coverage because of the high pressure necessary at 0°.

The calorimeter design has been described previously.¹⁴ Differential heats were measured using a single junction copper-constantan thermocouple, the voltage being amplified by a Perkin-Elmer D.C. breaker amplifier and recorded on an Esterline-Angus pen recording voltmeter. Calibration was effected by supplying electrical energy to the calorimeter through a heating coil. In the experiments on ammonia-Spheron (2700°), the calorimeter was employed "adiabatically" as described previously.² Operation in this fashion minimizes errors due to heat losses and gives highly reproducible results. Temperature control of a -78° bath with the precision necessary for calorimetry was found to be more difficult than for work at 0° or at -195°. However, satisfactory results were obtained when the cold junction of the thermocouple was surrounded by alternate layers of metal conductor and insulating material. Before starting an experiment, the calorimeter was allowed to remain overnight to attain temperature equilibrium. The overall accuracy of heat measurements obtained with this design of calorimeter is estimated to be about $\pm 3\%$. In the case of ammonia adsorption at 0°, the accuracy is probably less because of the relatively large correction for unadsorbed gas. Correction of the measured heats for the heat of compression of the gas within the calorimeter was shown to be negligible, as was also true for sulfur dioxide;^{2, 15} this statement is especially applicable to ammonia at -78° where P_0 is only 4.1 cm.

RESULTS

Ammonia isotherms on each of the three carbon blacks studied are compared in Fig. 1 for adsorption at -36.3° and in Fig. 2 for adsorption at -78.8°. It is

observed that the parent carbon black, Spheron 6, adsorbs appreciably more ammonia than the heat treated samples and this effect is more marked for adsorption at the higher temperature. The decline in adsorptive capacity with sintering parallels qualitatively the loss in surface oxygen complex.² Desorption hysteresis is present for both Spheron and Spheron (1000°) at -36.3° but uptake on the comparatively uniform oxygen-free surface of Spheron (2700°) is completely reversible. No desorption measurements were made at -78.8° on account of the low equilibrium pressure. Fig. 3 shows isotherms for ammonia adsorption on Spheron (2700°) at four different temperatures. In each case the isotherms are reproducible. The increase with temperature of the volume adsorbed at a given relative pressure is surprising and its significance will be discussed in a later section.

In Figs. 4-6 we have plotted, as a function of coverage, the calorimetric heats of adsorption for ammonia at -78° on the three carbon blacks. Calorimetric results for ammonia-Spheron (2700°) at 0° are given in Fig. 7. In view of the negligible correction for the heat of compression as mentioned above, the calorimetric heat values in Figs. 4 and 5 and in Curve 1 of Fig. 6 are identical with isosteric heats. Because of the highly uniform, graphite-like structure of the Spheron (2700°) surface and because this adsorbent was essentially free from any material other than carbon, the calorimetric data for the ammonia-Spheron (2700°) system was analyzed with special care.

The isotherm and the heat-coverage curve for adsorption of methylamine on Spheron (2700°) are shown in Figs. 8 and 9 respectively. No measurements were made of methylamine adsorption on Spheron or Spheron (1000°).

DISCUSSION

I. Adsorption of Ammonia on Spheron

The isotherms of Figs. 1 and 2 show that the original carbon black, Spheron, is capable of adsorbing appreciably more ammonia than the heat treated material. As the degree of graphitization increases through the series Spheron, Spheron (1000°), Spheron (2700°), the shape of the ammonia isotherm changes progressively from a characteristic Type II isotherm to one that is convex to the pressure axis at low pressures. Similar though somewhat less pronounced effects are observed with sulfur dioxide.² In the case of the nonpolar molecule argon, heat treatment of the carbon black has comparatively little effect on the amount adsorbed at a

given relative pressure, although here the increasing uniformity of the surface is reflected by a minor change in the isotherm shape.¹ We have tentatively ascribed the enhanced adsorption of sulfur dioxide by Spheron, compared with that by graphitized carbon black, to orientation of the dipoles of the adsorbate by the polarising surface, although the possibility of chemisorption on the surface oxygen is not discounted.

Comparison of the ammonia and sulfur dioxide adsorption data on Spheron reveals two points of difference: (1) there is a distinct hysteresis in the ammonia isotherm* not present for sulfur dioxide to any marked degree, (2) after an initial sharp drop, the heat of adsorption of ammonia on Spheron remains relatively constant at 8-9 kcal. per mole up to a surface coverage of 15 cc. per g. (see Fig. 4). With sulfur dioxide, the heat of adsorption on Spheron falls steadily with increasing coverage. Taken together, these two aspects of the ammonia data suggest that this gas is bound to the surface oxygen by some type of chemical complex rather than by simple physical adsorption of polar molecules on a polarising surface. It is known that the oxygen complex present on the surface of Spheron is acidic in nature and adsorption of a basic anhydride such as ammonia may well correspond to a neutralization of the surface or "salt formation". Certainly, the influence of surface oxygen complexes on porous charcoal in increasing the adsorption of alkali from solution has been fully established.¹⁶

Anderson and Emmett¹⁷ also have studied the adsorption of ammonia on carbon black and, like us, find considerably more adsorption on Spheron than on a heat treated Spheron from which most of the chemisorbed oxygen has been removed. This they attribute to solution of the ammonia in the surface oxygen complex with possible formation of hydrogen bonds. Such an explanation is not unreasonable as the unsymmetrical N-H- - -O hydrogen bond is often found in organic compounds. Moreover, recent work by Ellison, Fox, and Sizman¹⁸ has shown that hydrogen bonding of adsorbate molecules to surfaces, forming complexes of the type N-H- - -F, -O-H- - -F, is a real phenomenon.

While our present results do not serve to elucidate fully the mechanism of ammonia adsorption on Spheron, largely because of the uncertain and complex com-

* This effect was found on the -36.3° isotherm; no desorption points on Spheron were measured at any other temperature, e. g. -78°.

position of the surface, nevertheless the above considerations suggest that the mechanism is quite different from that responsible for sulfur dioxide.

II. Adsorption of Ammonia on Spheron (2700°).

At all temperatures we have studied, ammonia isotherms on Spheron (2700°) have the general form shown in Fig. 1. The isotherm is initially convex to the pressure axis at low surface coverages and then rises steeply, passing through a point of inflection at a relative pressure of 0.5 - 0.7. A qualitatively similar isotherm has been reported by Pierce and Smith¹⁹ for the adsorption on Graphon of methanol which likewise is a hydrogen bonded substance. This shape of isotherm differs from any of the five usual types classified by Brunauer²⁰ and was therefore designated Type VI.

Smith and Pierce have also studied the adsorption of ammonia on graphite.²¹ Here again the isotherms are of Type VI, but, because of the small surface area of graphite [4.0 sq. m. per g. compared with 84 sq. m. per g. for Spheron (2700°)] and the correspondingly small volume of gas adsorbed, the point of inflection was overlooked at first and the isotherms reported as Type III. In a later paper, in which Type VI isotherms for methanol were reported,¹² the same authors pointed out that the ammonia isotherms as well were actually of Type VI. The above authors identified the point of inflection as representing the completion of a monolayer and the amount of methanol adsorbed at this point agreed well with the computed value of V_m based on nitrogen surface area measurements and on an area of 16.2 sq. Å. for the methanol molecule. In the present investigation of the adsorption of ammonia on Spheron (2700°), the point of inflection varies considerably with the temperature at which the isotherm was determined. The value of V_m , estimated from the point of inflection, is of the same order as that expected for a close-packed monolayer based upon liquid density measurements, but more detailed considerations do not appear to be warranted.

The isosteric heats for ammonia-Spheron (2700°) shown in Fig. 6 are particularly interesting and unusual in two respects: (1) they are nearly constant at all coverages and (2) they are nearly equal to the heat of vaporization of ammonia. These observations can be explained on the basis of a model in which adsorption is initiated on relatively few active centers, and proceeds by the formation of adsorbed patches, one molecule in thickness, around these centers. Since the forces operative in holding a monolayer of ammonia to a carbon surface are by

no means identical with those in the bulk liquid ammonia, it appears to be fortuitous that the heats of adsorption and of vaporization have virtually the same value.* However, the two systems under consideration do have the common feature that hydrogen bonding is present to a large degree in each. It is therefore of interest to form an estimate of the percentage to which hydrogen bonding contributes to the heat of vaporization and to the heat of adsorption.

It is generally accepted that hydrogen-bonding contributes heavily to the total binding energy in bulk ammonia whether solid or liquid. Using the method of Pauling²² it is possible to estimate the contribution of van der Waals attraction and of hydrogen-bonding in solid ammonia at -78° as 2.6 and 4.8 kcal. per mole respectively out of a total heat of sublimation of 7.4 kcal.** Thus the hydrogen bond energy represents 65% of the heat of sublimation. We are not aware of a suitable method for calculating the percentage contribution of hydrogen bonding to the heat of vaporization of liquid ammonia at -78° . However, it seems probable that it would be of the same order of magnitude as in the solid state although possibly somewhat less. Thus it is reasonable to estimate that hydrogen

* In comparing the heat of adsorption with the heat of vaporization, it appears to be more valid from a thermodynamic point of view to correct the isosteric heats to equilibrium heats, as defined by Hill,²³ at constant value of ϕ the spreading pressure. The equilibrium heats have been calculated for the system ammonia-Spheron (2700 $^{\circ}$) at -78° and they are shown in Fig. 6. In making this calculation the percentage error in the pressures must be small in order to avoid large errors in evaluating the spreading pressure, a quantity which is required in calculating the equilibrium heats. It may be seen from Fig. 2 that, because of the shapes of the isotherms, the percentage error in the pressure for any given coverage would be much less in the adsorption of ammonia on Spheron (2700 $^{\circ}$) than on the other blacks. Because of this and because the more fundamental nature of the surface of Spheron (2700 $^{\circ}$), the calculation of equilibrium heats has been limited to the data on this latter adsorbent.

** The value used by Pauling for the total heat of sublimation of ammonia is believed to be in error. The heat of fusion of ammonia at -78° is 1.3 kcal. per mole. Fig. 10 shows that the heat of vaporization at that temperature is 6.1 kcal. per mole giving a heat of sublimation of 7.4 kcal. per mole. Pauling's value of 6.5 kcal. per mole is based upon the heat of vaporization at the boiling point. During fusion, some of the hydrogen bonds present in the solid are broken. Further bonds are disrupted on warming the liquid to the boiling point. By using the value of 5.2 kcal. at the boiling point, Pauling does not include the latter in his calculation.

bonding would contribute from 50 to 65% of the total binding energy in the liquid state.

It seems probable to us that hydrogen bonding is likewise an important factor in the total energy of binding in the ammonia film on the carbon surface. In fact, we estimate that van der Waals attraction of the surface for ammonia molecules probably contributes no more than 50% of the heat of adsorption. This estimate is based on the following reasoning. We assume that there is virtually no oxygen on the Spheron (2700°) surface. Thus the only attraction between the surface and any adsorbed ammonia molecules would be due to van der Waals forces. Previous work in this laboratory has shown that the heat of adsorption of n-butane on Graphon, a carbon adsorbent which is essentially the same as Spheron (2700°), is 8-9 kcal. per mole.²⁴ It seems justifiable to assume that the molecules of n-butane are adsorbed with their major axes lying in the plane of the adsorbing surface.²⁵ Thus, each $-CH_2$ or $-CH_3$ group would contribute about one fourth of the heat of adsorption or approximately 2.2 kcal. per mole. It is reasonable to assume that the van der Waals attraction of the carbon surface for ammonia (molecular weight 17) would be roughly the same as that for $-CH_2$ (molecular weight 14), although molecular configuration would doubtless be a contributing factor. Suppose we assume a van der Waals attraction of 3.0 kcal. per mole for ammonia to the carbon surface; this leaves an additional 3.0 kcal. which must be accounted for as lateral interaction between adjacent adsorbed ammonia molecules. It seems probable that lateral interaction of this magnitude must be due in large part to hydrogen-bonding of adjacent ammonia molecules. Moreover, since the heat of adsorption is almost 6.0 kcal. per mole even at coverages as low as 2 cc. per g., it would appear that the high contribution (3.0 kcal. per mole) due to lateral interaction must be effective even on a relatively bare carbon surface. Such a set of conditions is satisfied by a model in which adsorption is initiated at relatively few active centers, but proceeds by the formation of patches around these centers.

The above model would differ from that which has been postulated for argon on a similar carbon surface¹ in which the surface presented to the argon a system of non-localized sites. With argon, lateral interaction becomes important only after the monolayer approaches completion.

The equilibrium entropy is readily obtained from the equilibrium heat. When regarding the system as a pseudo one-component system, i. e. adsorbate in the

force field of the adsorbent, then it is this integral entropy which can be related to statistical mechanical models. As Hill et al point out, the corresponding differential quantities may be totally misleading.²⁶ "Net" entropies with coverage are plotted in Fig. 11. It may be seen, that adsorption of the first two cubic centimeters of ammonia is accompanied by a steep decrease in the equilibrium entropy curve, showing decreasing randomness of motion of the adsorbed molecule. From then on a more gradual decline towards a minimum near the completion of the first layer indicates a relatively smaller change in molecular order with coverage. As is to be expected, maximum order is to be found near the completion of the first layer.

III. Adsorption of Ammonia on Spheron (1000°)

Heat treatment of Spheron at 1000° is known to remove most of the chemisorbed oxygen, while X-ray studies show that little graphitization has taken place at this temperature.^{2, 11, 12} In these respects Spheron (1000°) stands in a position intermediate between Spheron and Spheron (2700°). This intermediate position is reflected in the isotherms of Figs. 1 and 2 and in the heat curves of Figs. 4, 5, and 6. This relative behavior of ammonia on the three blacks is very similar to that previously observed for sulfur dioxide.² In comparing the isotherms for the three blacks, we should remember that nitrogen surface area determinations give evidence of a decrease in specific surface area with increasing temperature of graphitization. However the relative positions of the isotherms in Figs. 1 and 2 are not appreciably altered if the ordinates are plotted as cc. per sq. m. of surface rather than cc. per g.

It is interesting to note from Fig. 5 that most of the sites in the parent Spheron, capable of adsorbing ammonia with a heat higher than 8 kcal. per mole, have been destroyed by heat treatment at 1000°. After the first 3 cc. per g., any further adsorption produces heats which are only slightly greater than those observed in the most highly graphitized sample, Spheron (2700°). Since little graphitization has occurred at 1000°, the above observations confirm our previous conclusion that the high heats on the Spheron as shown in Fig. 4 are due to reaction of the ammonia with surface oxygen complex rather than to simple physical adsorption on the Spheron surface.

IV. Adsorption of Water on Graphon

It is of interest to contrast the results for the adsorption of ammonia on Graphon with those for water vapor. Water, like ammonia, is a low molecular weight, hydrogen bonded substance. Yet adsorption of water vapor on the oxygen-free, non-

porous carbon is virtually absent at room temperature below a relative pressure of 0.9 or higher. In fact, Graphon may be classified as a hydrophobic surface. In this respect, ammonia differs from water as is seen from Fig. 1. Simple physical adsorption of single water molecules (molecular weight 18) would not normally be expected at room temperature to any appreciable degree. Although water is strongly adsorbed at low relative pressure on many solids, the mechanism in such cases is invariably one of chemisorption, hydration of ions, capillary condensation, or hydrogen bonding to the surface. It is probable that adsorption of water on silica gel, for example, takes place by forming $O - H - -O$ bonds with the surface. Such adsorption of discrete molecules would explain why the magnetic susceptibility and microwave adsorption technique gave no evidence of hydrogen bonding between water molecules. On a uniform, inert surface where the possibilities for the above mechanism of adsorption do not exist, water is not appreciably adsorbed, except at very high relative pressures. Droplets of water will not spread on these nonpolar surfaces but form finite angles of contact. The contrast with ammonia uptake on Spheron (2700°) is marked. It appears that adsorption of water with lateral hydrogen bonding between adjacent molecules does not readily occur. The reason for this is not at once apparent, but may be associated with the relatively high energy of the $O - H - -O$ bond (4.5 kcal. per mole) and the open tetrahedral configuration of hydrogen bonded water.²² Ammonia, by comparison, is weakly hydrogen bonded and may have an almost close-packed structure. In order for a nucleus of adsorbed water to grow laterally in a monolayer on a uniform surface, a marked distortion of the strong $O - H - -O$ bonds would be necessary. With ammonia, the weaker $N - H - -N$ bonds may be more readily distorted under the combined influence of the surface and the neighboring adsorbed molecules.

Recent heats of wetting measurements by Zettlemoyer et al.⁴ for water-Graphon and by Bartell and Suggitt⁵ for water-graphite have shown that the net heat of adsorption at low coverage is negative in these cases; i. e. the calorimetrically measured heat of adsorption is less than the heat of vaporization. As we have mentioned previously, it is more justifiable in comparing heats of adsorption with heats of vaporization to consider equilibrium heats of adsorption at constant spreading pressure. However, it is noteworthy that a specific adsorption type is characterized by the sign of the net heat of adsorption. Thus, as we go from a Type II isotherm as typified by nitrogen and argon on Graphon through intermediate Stages (ethyl chloride,²⁷ methanol,¹⁹ sulfur dioxide² and ammonia on Graphon) to a

Type III isotherm (water-Graphon)²⁸ the net heats of adsorption shift from strongly positive to definitely negative values. It happens that ammonia-Graphon illustrates an intermediate stage where the net heat of adsorption is virtually zero.

V. Adsorption of Methylamine on Spheron (2700°)

The isotherms for adsorption of ammonia and methylamine on Spheron (2700°) and methanol on Graphon resemble each other in being of Type VI. These are the only three examples of Type VI isotherms so far reported and it will be observed that each of the adsorbates is a substance which is hydrogen bonded in the liquid state.

The heat-coverage curve for methylamine on Spheron (2700°) differs from that for ammonia in that the heat rises somewhat with coverage and passes through a maximum. In this respect, the curve is similar to that for sulfur dioxide adsorption. The maximum heat value for methylamine occurs at a coverage of about 17 cc. per g. which corresponds with the rather ill-defined point V_m from the isotherm (16 ± 1 cc. per g.). Similarly, in the case of sulfur dioxide adsorption, the maximum heat value is found at about the same coverage as the point V_m . However, this coverage is somewhat less than that necessary for a close packed monolayer and entropy considerations suggest that second layer formation commences before a monolayer is completed. It is important to observe that the isotherms for both ammonia and methylamine, which are adsorbates capable of hydrogen bonding, do show a point of inflection somewhere in the region of monolayer coverage. This is strong evidence¹⁹ that hydrogen bonding is largely confined to two dimensions between adjacent adsorbed molecules and that three dimensional bonding, resulting in droplet formation, does not occur to any appreciable extent.

On the basis of heats of adsorption and isotherm measurements alone it is not possible to draw detailed conclusions concerning the mode of adsorption of methylamine, but this adsorbate does appear to stand in a position which is intermediate between ethyl chloride²⁷ and ammonia when adsorbed on an oxygen-free carbon surface.

VI. The Effect of Temperature on the Adsorption of Ammonia on Spheron (2700°).

The isotherms shown in Fig. 3 are rather unusual in that adsorption increases with increasing temperature at a given relative pressure. Several examples of this phenomenon are to be found in the literature, but so far as we are aware, the examples are limited to the adsorption of either water vapor or ammonia on carbon surfaces. Coolidge²⁹ was the first to observe this effect in the case of water

adsorption on an ash-free charcoal carefully prepared from recrystallized cane sugar. He found an increase in adsorption with temperature over the range 60° to 218° in the relative pressure region 0 to 0.3; but the isotherms at 20° to -30° were coincident. In discussing the significance of his observations Coolidge makes the following comments.

"These relations become very interesting when we consider their bearing on the energy changes involved. The 'net heat of adsorption' or heat of transfer from free liquid to adsorption may be obtained by substituting the relative for the absolute pressure in the Clapeyron equation. The distance between two isotherms, measured along a line of constant concentration, evidently indicates the sign and magnitude of the net heat. More accurate values may be obtained from the slopes of the isosteres as directly determined, but the qualitative relations are more easily apprehended from the isotherms. The net heat is zero when the relative pressure is the same at different temperatures, which is true for low concentrations between -30° and 20° . Above 20° it is negative, decreasing rapidly as the temperature rises. This would seem to be the first case in which the total heat of adsorption has been found to be less than the heat of vaporization."

Pierce and Smith³⁰ found that the isotherms for water-Graphon were coincident at 0° and 28.6° up to 0.9 relative pressure. Following the suggestion of Coolidge, these authors conclude that their isotherm data indicates a zero net heat of adsorption. In a later paper, Pierce et al²⁸ reported that water adsorption was considerably increased by raising the temperature from 28.6° to 80° . However, these investigators showed that a reaction occurs between water vapor and Graphon at all temperatures throughout the range 25° to 150° . They make the reasonable suggestion that this reaction between the water and the carbon produces a C-O complex on the surface, which is known to adsorb water better than a clean carbon surface. They therefore conclude that the large negative value of $E-E_L$ which appears to be indicated by the comparison of the 80° and the 28.6° isotherms is spurious, since the isotherms are not on the same surface.

In the system ammonia-Spheron (2700°) we have no evidence of any chemical reaction between the ammonia and the carbon surface in the temperature range studied (-78° to 0°). Certainly no oxygen complex is formed by reaction of the ammonia with the surface. Thus the observation that adsorption increases with temperature at constant relative pressure must be considered as evidence of a real phenomenon. Moreover, the calorimetric heats of adsorption at -78° are, within the experimental error, equal to the heat of vaporization. If we follow Coolidge's suggestion that our isotherms over the range -78° to 0° should indicate negative

net heats of adsorption as calculated by means of the Clapeyron equation, there is an apparent discrepancy between the isosteric and the calorimetric heats.

We believe the explanation of the above apparent discrepancy to be as follows. The conclusion that the net heat of adsorption is negative, if the equilibrium relative pressure decreases with increasing temperature, follows from the following mathematical expression:

$$(q_{st.} - E_L) = R \frac{T_2 T_1}{T_1 - T_2} [\log P_1/Po_1 - \log P_2/Po_2] \quad (1)$$

where $q_{st.}$ is the isosteric heat of adsorption and Po_1 and Po_2 are vapor pressures at temps. T_1 and T_2 respectively. This equation is obtained by combining the integrated Clausius-Clapeyron equation for liquid/vapor equilibrium with the analogous equation for adsorption and thus involves the approximations inherent in these integrated equations, viz: (1) $q_{st.}$ and E_L are independent of temperature and (2) $PV = RT$. In a case such as the present where the net heat of adsorption is close to zero, the variations in $q_{st.}$ or in E_L with temperature may well be large enough to reverse the usual order of the isotherms, giving apparent negative net heats.

In Fig. 10, the heat of vaporization of ammonia (E_L) is plotted as a function of temperature. Values of E_L were calculated from the Clausius-Clapeyron equation in differential form,

$$dP/dT = E_L/T (V_g - V_L) \quad (2)$$

using well established data for the vapor pressure and specific volumes of ammonia.³¹ At the boiling point (-33.4°), the heat of vaporization so calculated (5.57 kcal. per mole) agrees well with direct calorimetric observations of Overstreet and Giaque (5.58 kcal. per mole)³² and of Osborne and Van Dusen (5.57 kcal. per mole).³³ Use of the integrated form of the Clausius-Clapeyron equation, involving the perfect gas assumption, gives a value for E_L at the boiling point which is over 100 cal. too high. The variation of E_L with temperature in the range in which the isotherms were measured (-22° to -78°) is as much as 660 cal. or about 11%.

It is necessary to bear in mind that, in Equation 1, it is a variation with temperature in the quantity $q_{st.} - E_L$ which could produce a reversal of the usual order of the isotherms although the calorimetrically measured net heat may be virtually zero. Of course, there is no reason to believe that the quantities $q_{st.}$ and E_L would have the same kind of temperature dependence and thus $q_{st.} - E_L$ may well vary appreciably with temperature. Our calculations, based on Equation 1,

show that a variation of a few per cent, over the temperature range under consideration, in the quantity $q_{st.} - E_L$ would be sufficient to cause a reversal of the usual order in the isotherms. It seems probable that these considerations would be especially applicable to hydrogen bonding substances like water or ammonia. It is reasonable to expect a high temperature coefficient of both the heats of vaporization and of adsorption because hydrogen bonds would be broken as a result of the increased thermal agitation with increasing temperature.

Because of the above considerations it is not justifiable to make use of the integrated form of the Clapeyron-Clausius equation unless the value $q_{st.} - E_L$ is independent of temperature or unless T_1 and T_2 are close together. Equation 1 is being used in effect whenever the isosteric heat is calculated from data at two temperatures only. It is noteworthy that Carman and Raal³⁴ have found a negative net isosteric heat for ammonia on Sterling S carbon black from adsorption data at -33.1° and 63.5° . The net heat may actually be negative in this case, but we cannot be sure without more experimental data. There is of course no reason to exclude the possibility of negative net heats. They have been observed calorimetrically for the systems water-Graphon⁴ and water graphite⁵. From the work of Pierce et al.^{30, 35} it seems probable that Coolidge may have had some reaction between water vapor and his sugar charcoal to produce C-O complexes on the surface and thus account for the higher adsorption of water at higher temperature. On the other hand, there may have been very little chemical reaction with water on Coolidge's charcoal surface and his reversed order of the water isotherms with temperature may be a true phenomenon as is the case with our ammonia-Spheron (2700 $^\circ$) system. In light of our above discussion of the relation between isosteric heats and the isotherms, it is evident that such a reversed order, even if real, could not be used as evidence either for or against negative net heats for Coolidge's water-carbon system.

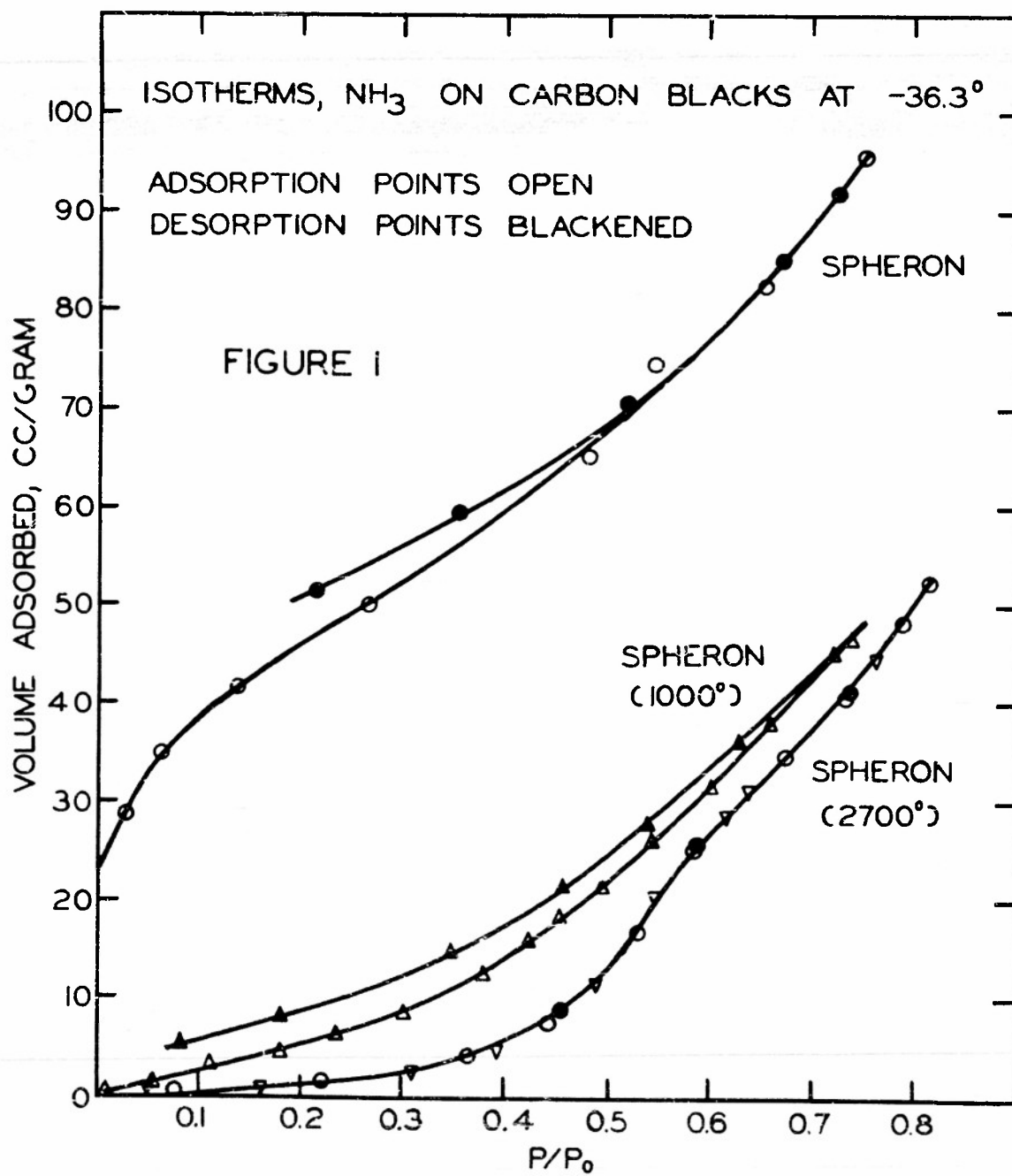
In most laboratories it is now customary in determining isosteric heats of adsorption to plot the functions $1/T$ against $\log p$ at fixed coverages. For this purpose adsorption data is obtained for three or more different temperatures. The heats of adsorption are then read off from the slopes of these plots. This method is based on the differential form of the Clapeyron-Clausius equation. It is fair to point out that Coolidge recommended this method as giving more accurate results. The point is that the use of Equation 1 (above) may give results which are so inaccurate as to be quite misleading.

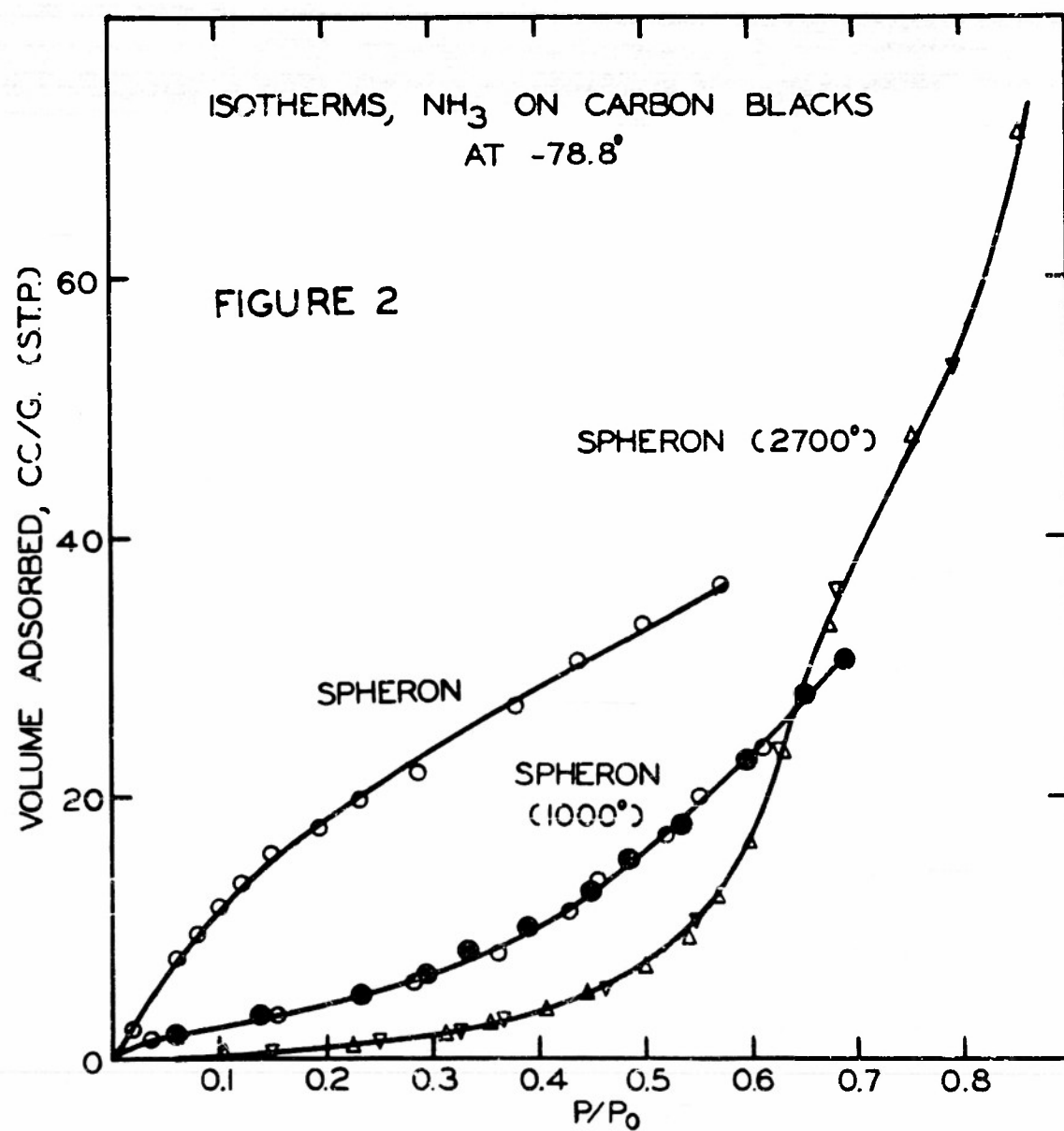
Acknowledgement -- Our thanks are due to Mr. Leonard Berkan for assistance in determining the isotherms and to Mr. John Fuller for help in constructing the apparatus. We are especially indebted to Dr. Carl Amberg for helpful discussions in the interpretation of the results.

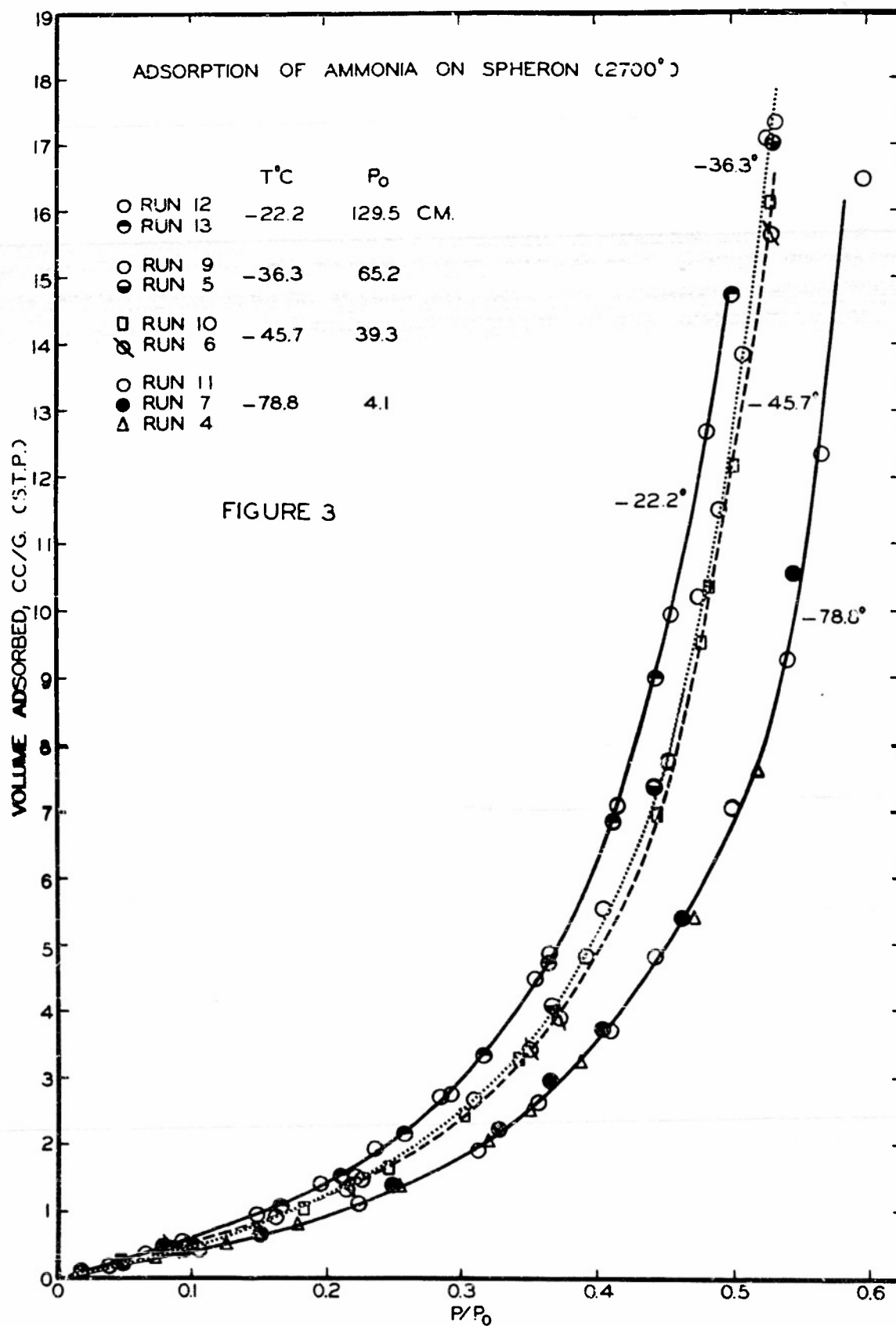
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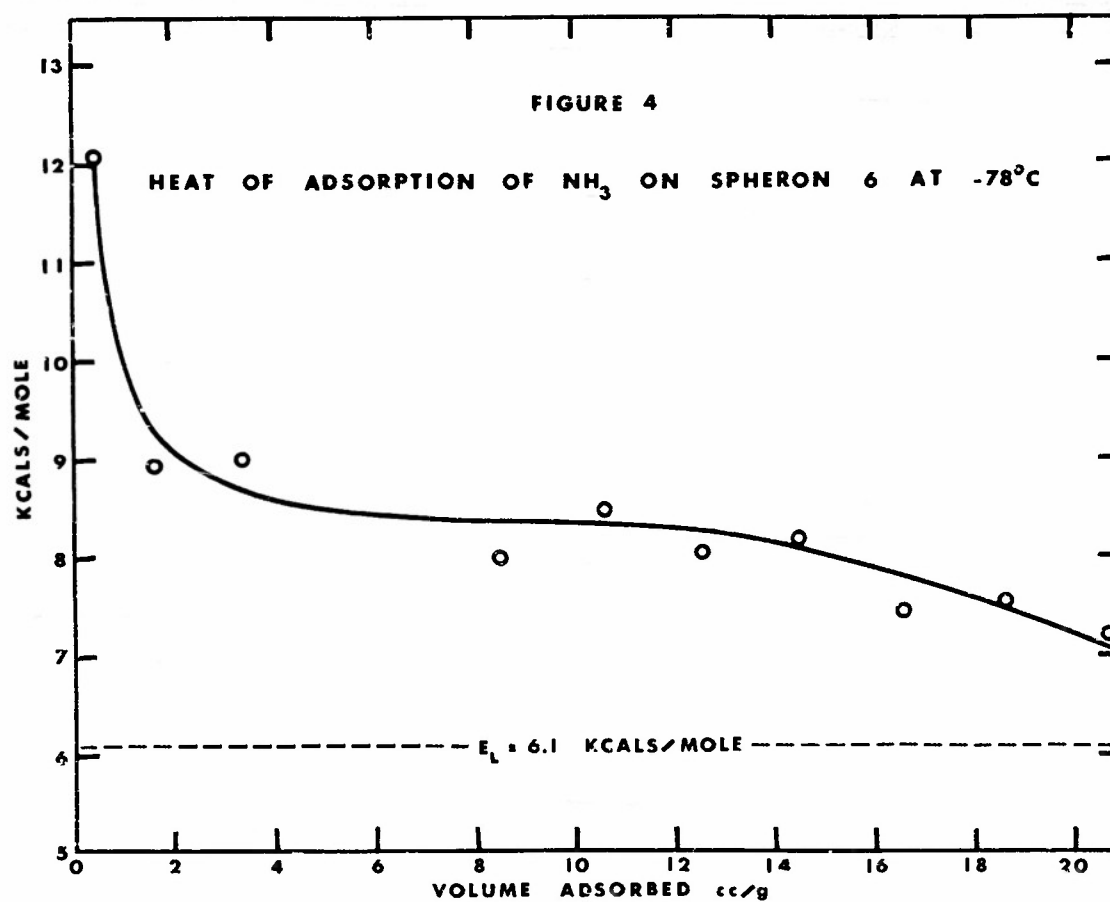
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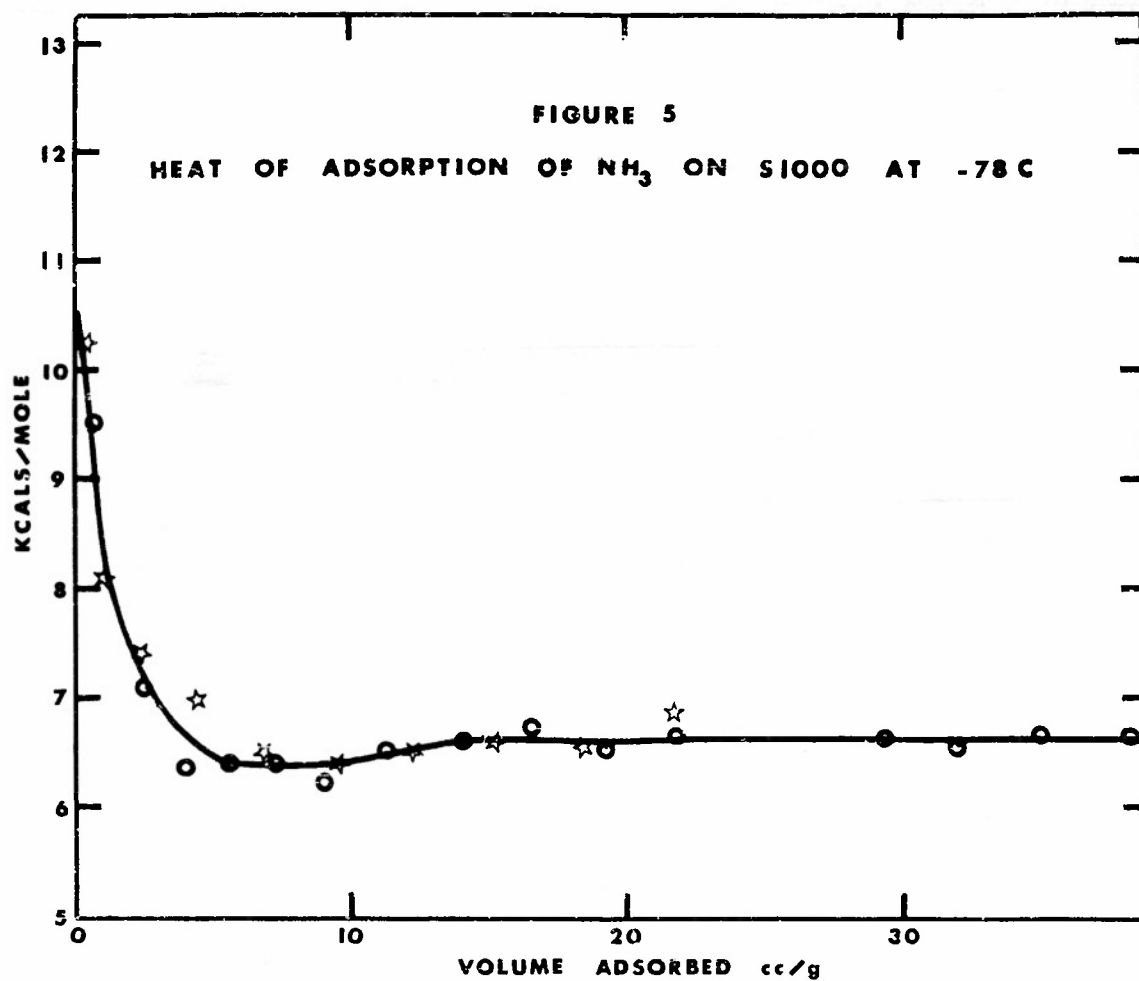
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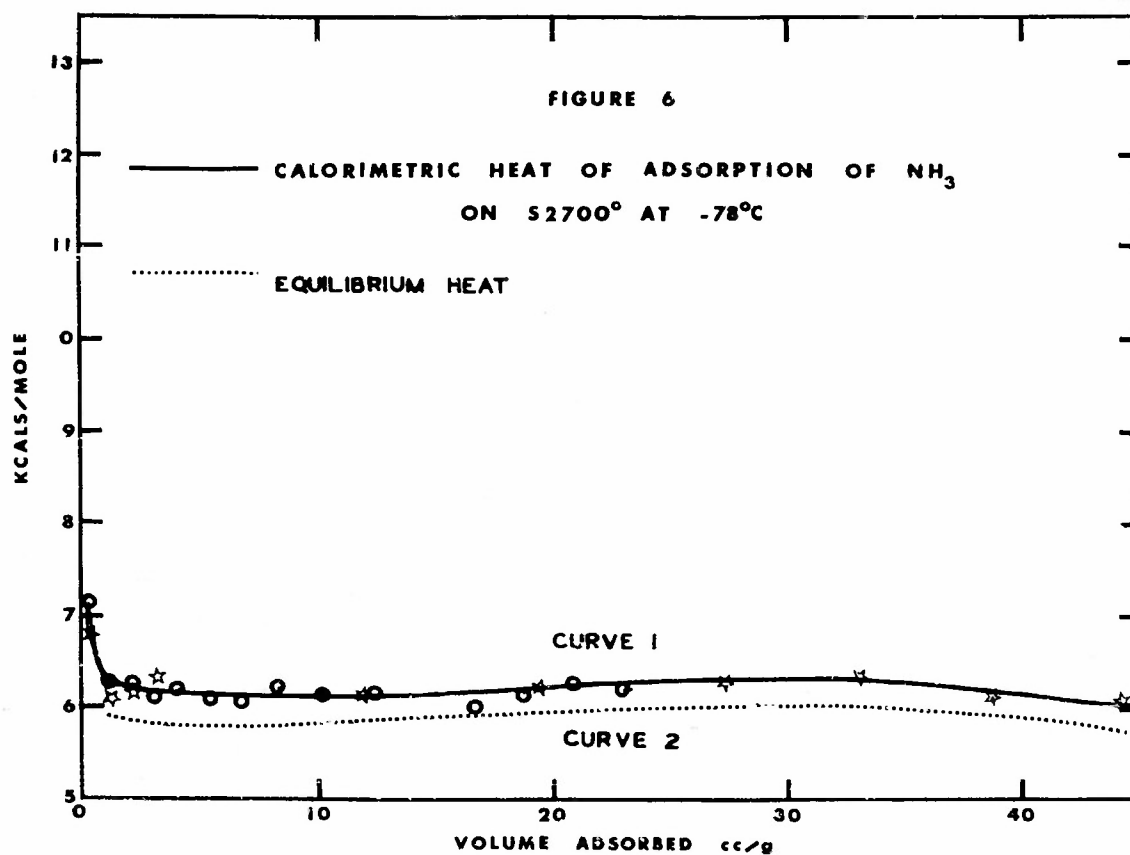


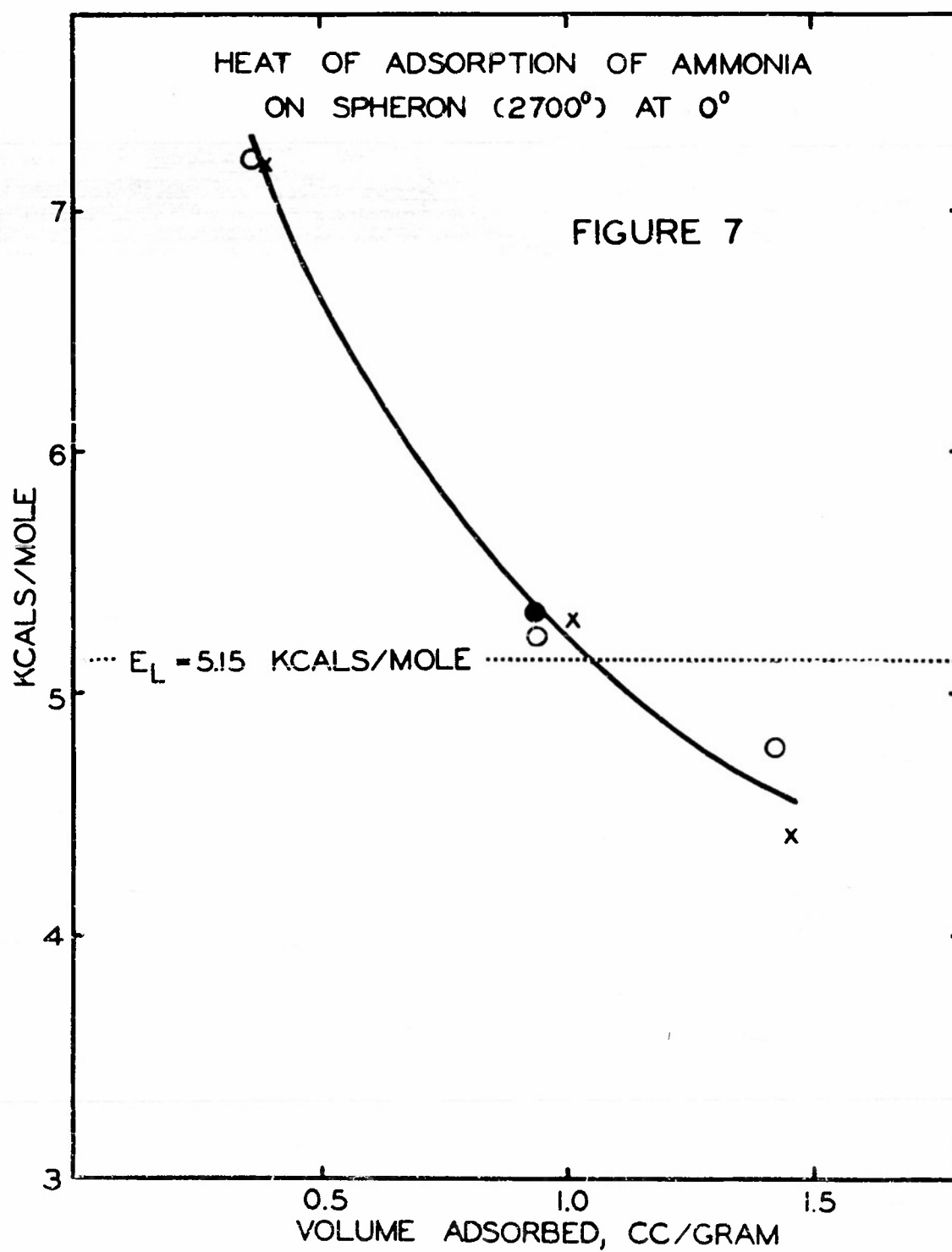


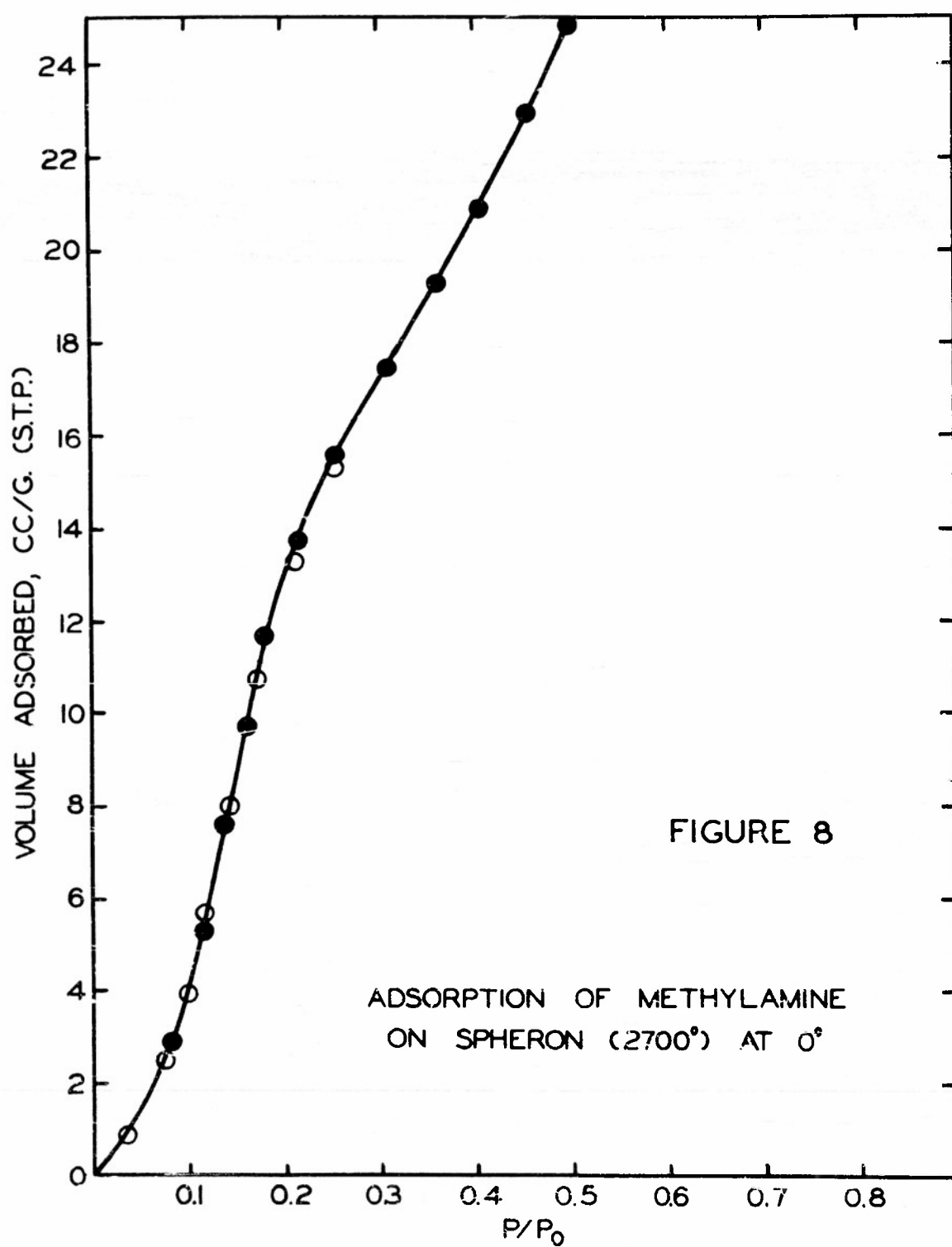






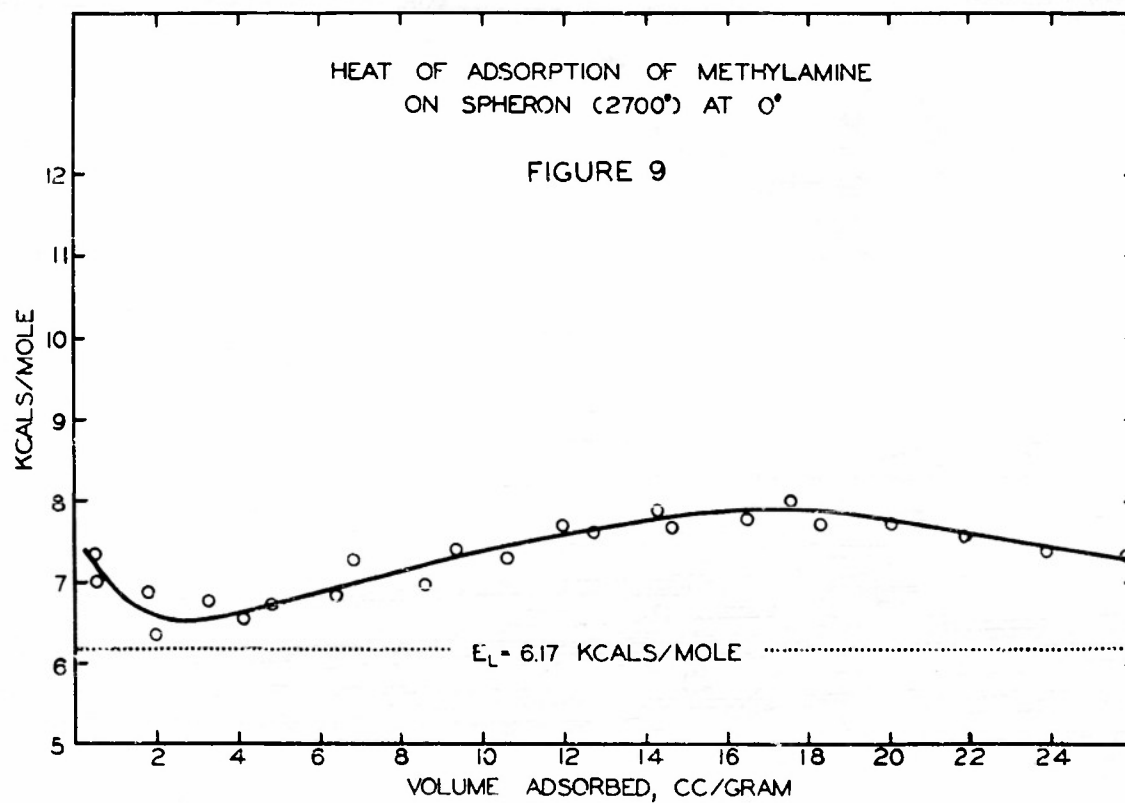


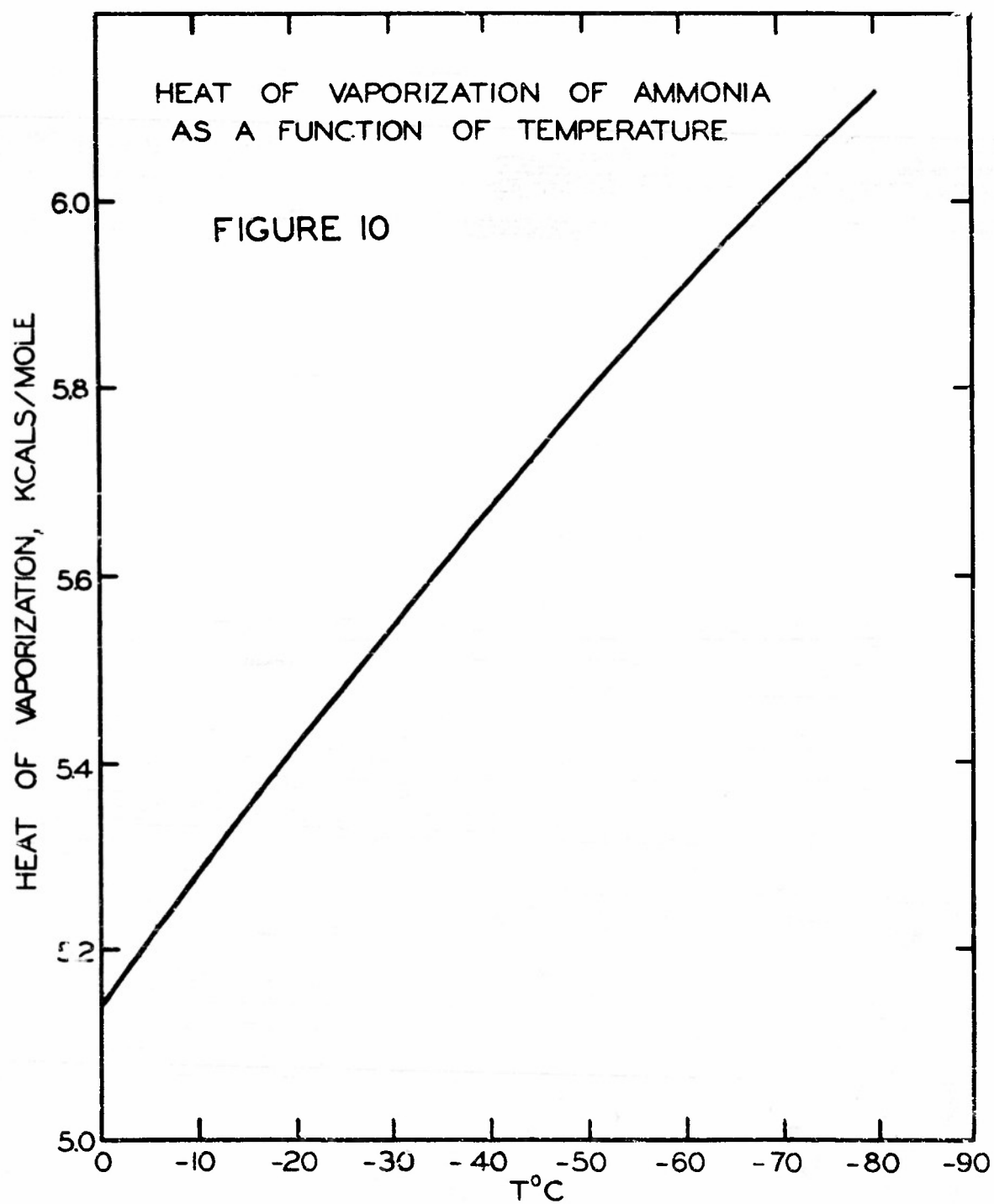


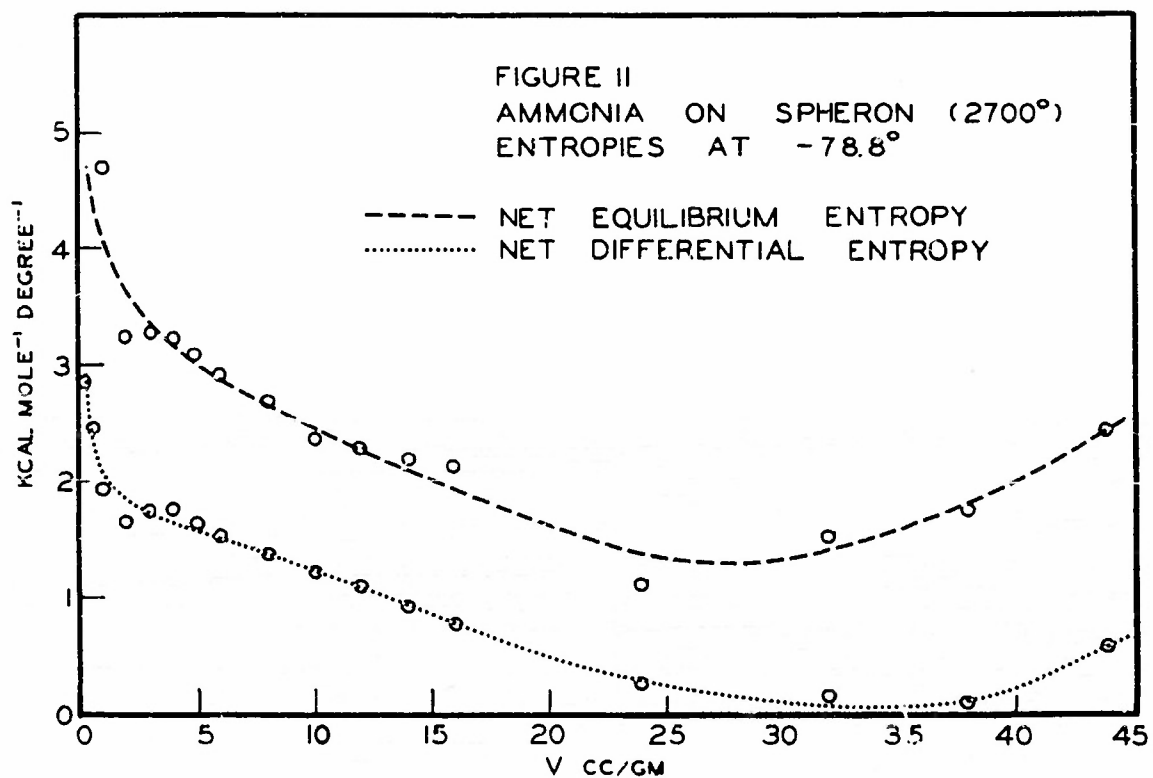


HEAT OF ADSORPTION OF METHYLAMINE
ON SPHERON (2700°) AT 0°

FIGURE 9







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