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HETEROGENEITY OF SURFACES

Immersion Calorimetry and
Adsorption Studies
of

The Heterogeneous Nature of
Nickel and Carbon Surfaces

Project Supervisor A. C. ZETTLEMOYER

Investigators - J. J. CHESICK, F. H. HEALEY, Y. YU

Office of Naval Research
Technical Report Number 6
1 June 1953 to 31 May 1954

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Project Number
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The Surface Chemistry Laboratory
Lehigh University
Bethlehem, Penna.

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ABSTRACT

I. Isotherms for the adsorption of argon on oxide-coated nickel powder and on this sample after each of several reductions with dry hydrogen at 350° were determined at -195° and -183°. Equilibrium functions, isosteric heats of adsorption and integral molar entropy values were calculated. These data showed a marked difference in the surface nature of the unreduced and reduced samples. However, the adsorption behavior of argon on the reduced samples was similar above monolayer coverage. In this region of adsorption the only effect of reductions at high temperature was to cause an increase in particle size due to sintering without markedly changing the surface nature of the reduced metal powder.

The equilibrium function and isosteric heat data indicated that both the unreduced and reduced samples were heterogeneous. Adsorption sites of higher energy as well as a wider distribution of sites characterized the unreduced samples. Stronger cooperative effects leading to an increase in heat values and a subsequent maximum near monolayer coverage was found for argon adsorption on the reduced sample.

On the basis of experimental and calculated integral entropy values, a model of localized adsorption on a heterogeneous surface without adsorbate interactions explains the adsorption of argon on the unreduced and reduced sample. This model is probably not valid beyond $\theta = 0.5$ for the unreduced sample and beyond the relatively low value of $\theta = 0.2$ for the reduced sample; above these θ values lateral interaction set in. At very low coverages on both samples the heterogeneous nature of the surfaces was evident from the low molar entropy values S_g and small configurational entropy contributions.

II. A low temperature calorimeter to measure heats of immersional wetting in liquid nitrogen, has been constructed. The heats of immersion of magnesia, silene, alumina and Graphon (a graphitized carbon black) in liquid nitrogen were found to be practically the same. Thus, a simple determination of the heat evolved in terms of the volume of liquid nitrogen vaporized when the clean solid is broken under the liquid may be used to measure specific area.

Theoretical values for the heat of immersion of magnesia in liquid nitrogen have been calculated by two methods from adsorption data, and were found to compare favorably with the experimental value. The contribution of the free energy term to the heat of immersion was approximately one-third that of the $T\Delta S$ contribution.

III. The effect of increasing the amount of surface oxide on Graphon on both the water vapor adsorption isotherms and the heat of immersion in water was studied. Oxidations were carried out at 530°C with both dynamic and static oxygen atmospheres for successive periods up to 20 hours total. While the volume of water adsorbed increased regularly with the time of oxidation, the shape of the isotherm up to a relative pressure of 0.6 remained unchanged; plots of surface coverage vs. relative pressure were identical for the original sample and for the various oxidized samples.

The weight loss due to formation of volatile oxides of carbon was a linear function of time of oxidation whereas the formation of surface oxide appeared to follow a parabolic rate curve. The ratio of the apparent area available to water adsorption to the total area of Graphon determined by nitrogen adsorption was taken as a measure of the fraction of surface oxidized. After activation for two hours at 900°C the sample showed a considerable decrease in the number of hydrophilic sites due to volatilization of oxygen complexes on the surface of the original sample.

The heat of immersion in water did not prove to be a linear function of the fraction of hydrophilic surface. The increasing slope of the heat of immersion vs. hydrophilic fraction appeared to indicate that interactions between molecules adsorbed on adjacent patches of oxide sites increased as the number of patches on the surface increased. The slope and intercept of the curve for the more hydrophobic samples was used to estimate the heat of wetting of the carbon surface and of the hydrophilic sites.

GENERAL INTRODUCTION

The investigation of surface heterogeneity in this laboratory has demonstrated that a metallic surface may have both a real physical heterogeneity due to surface irregularities and an apparent chemical heterogeneity due to changes in the work function of the metal during the adsorption process. In addition, heterogeneities of particular importance in chemisorption result from the presence of chemical impurities on the surface of the adsorbent. These three types were shown (Technical Report No. 4) to be important to an understanding of the behavior of molybdenum towards oxygen at low temperatures.

The studies of Graphon (Technical Report No. 5) by gas adsorption and also by a newly developed immersional calorimetric technique illustrated the role of active sites in the adsorption process even though they are only sparsely distributed on the surface. Without the development of the immersion calorimeter, the thermodynamic data necessary for the elucidation of the mechanism of water adsorption on Graphon would have been impossible. Furthermore, the combination of adsorption and calorimetric measurements greatly widens the range of solid systems that can be studied. Thus, a previous study of the oxide films on nickel, steel, and molybdenum (Technical Report No. 5) illustrated the value of heat of immersion data in obtaining a quantitative measure of the porosity and hydrous nature of oxide coatings. For asbestos,

the linearity of the heat of immersion curve with increasing amount of water preadsorbed provided elegant confirmation of the surface homogeneity of this material.

The role of surface heterogeneities such as crystal edges, cracks, lattice defects, and grain boundaries in chemisorption is highly controversial. Wheeler (1) points out that

-
- (1) Structure and Properties of Solid Surfaces, Univ. of Chicago Press, Chicago, Illinois (1953) p. 458.
-

the possibilities of the properties of plane crystal surfaces and their role in chemisorption should be exhausted before heterogeneities should be invoked. Furthermore, a new concept of the process of chemisorption has been advanced by workers (2)(3) who seek the explanation for chemisorption in terms of

-
- (2) M. Boudart, J. Am. Chem. Soc. 74, 1531 (1952).
(3) D.H. Dowden, J. Chem. Soc., p. 242 (1950).
-

the band theory of metals, or more explicitly in terms of the changes in the Fermi level of the metal and the distribution and occupancy of the electron energy levels at the Fermi surface as chemisorption proceeds. Boudart's model accounts for the main facts of chemisorption without directly involving the presence of the usual types of surface heterogeneities although there exists

a marked similarity between this picture and that of "apparent" chemical heterogeneity defined in our Technical Report No. 5. Dowden's views are most complete since they include the effect of chemical and physical heterogeneities. In addition, Volkenshtein (4) has introduced the interesting idea that

(4) F.F. Volkenshtein, Zh. Fiz. Khimu. 23, 917 (1949).

heterogeneities are mobile and can interact. To assess the value of these new ideas a critical survey of the current data and theories of the role of surface heterogeneities in chemisorption was undertaken (presented at the Gordon Conferences on Corrosion and on Chemistry at Interfaces). A summary of this study will form the basis for a future technical report in this series. It may be categorically stated, however, that certain chemisorption results from this Laboratory, as well as data presented in the recent literature, could not be explained at present without recourse to the heterogeneity concept.

The present report contains three sections covering various phases of the project in manuscript form:

1. The results of a study of the heterogeneous nature of oxide-coated and reduced nickel samples by the adsorption of argon at low temperature.
2. A description of a newly designed and constructed immersion calorimeter used to obtain heats of wetting of solids

in liquid nitrogen and its application to a study of a sample of magnesia which had been extensively studied by adsorption methods.

3. A study of the system water-Graphon and the heterogeneities introduced by successive oxidations at high temperature.

A summary of work in progress is also included.

ADSORPTION STUDIES ON METALS IV.
THE PHYSICAL ADSORPTION OF ARGON ON
OXIDE-COATED AND REDUCED NICKEL

INTRODUCTION

Gas adsorption techniques were employed in this laboratory to study the surface heterogeneity of molybdenum metal (1). A thick oxide film was formed on the molybdenum

(1) F.H. Healey, J.J. Chessick and A.C. Zettlemoyer, J. Phys. Chem. 57, 178 (1953).

surface after exposure to moist air during storage. Reduction of this polymolecular oxide film by high temperature treatment with dry hydrogen increased the surface roughness or physical surface heterogeneity. After successive heatings in the presence of hydrogen a lower limit of surface area was reached. For a further understanding of metallic surface properties, this work has been extended to nickel.

Through the development of adsorption thermodynamics and its application to various adsorption systems in the last decade, it is now well established that thermodynamic functions are very useful for characterizing the properties of adsorbed films. However, since the complexity of the different existing forces and the wide differences in surfaces, it is helpful to investigate more than one function before reaching final conclusions. A sharp initial drop of the isosteric heat with increasing

surface coverage is generally attributed to the surface heterogeneity. Following Hill's (2) statistical development, the

(2) T.L. Hill, J. Chem. Phys. 17, 262 (1949).

entropy of the adsorbed phase could be evaluated, which serves as a parameter for defining a surface. Furthermore, Morrison and Drain (3) were able to calculate the configurational and

(3) J.M. Drain, J.A. Morrison, Trans. Faraday Soc. 48, 316 (1952).

non-configurational entropy values of system consisting of a heterogeneous surface. Recently, Graham (4) has introduced

(4) D. Graham, J. Phys. Chem. 57, 665 (1953).

the equilibrium constant of a localized adsorption system for characterizing a surface. Very little work has been done with the last method. In the present work the conclusions from this free energy function are compared to those of isosteric heats and entropies.

EXPERIMENTAL

Materials and Apparatus - The nickel sample furnished by the International Nickel Company had a reported purity when first prepared greater than 99%, and a particle size range from 2 to 25 microns. The sample was passed through a 400 mesh sieve before use to remove large particles.

High purity tank argon and helium were used. The argon was further purified by passage through fine copper gauze heated to 500°C and dried with magnesium perchlorate. Helium was purified by passage through a charcoal trap immersed in liquid nitrogen.

Tank hydrogen, 99.8% pure, was passed slowly through a Baker Deoxo Unit, containing a palladium catalyst, and then through a drying train consisting of two magnesium perchlorate driers, a phosphorous pentoxide tube and a cold trap immersed in liquid nitrogen. Previous work in this laboratory showed that water diffused into the reduction system if rubber connections were used. Therefore, the reduction system was of all-glass construction with Tygon tubing connections.

An Orr type (5) apparatus was used. Apiezon B oil which

(5) W.J.C. Orr, Proc. Roy. Soc. (London), 173A, 349 (1939).

had a very low vapor pressure and did not dissolve measurable amounts of the gases studied was used in the manometers. Pressures as low as 0.005 cm. Hg. were measured with this oil. However, the height of the manometer restricted pressure measurements to about

5 cm. Hg. To increase the range of the manometer, a back pressure was applied to the vacuum side of the manometer for pressures greater than 5 cm. Hg. In this way, adsorption pressures as high as 20 cm. Hg. were obtained.

It was shown previously (6) that samples with an area

(6) J.J. Chessick, Ph. D. Thesis, Lehigh University (1952).

as low as 0.5 m^2 could be studied with precision with this apparatus. Nevertheless, in this investigation sufficiently large samples were taken so that the total area ranged from 3 to 7 cm^2 .

Pretreatment of Samples - The unreduced, polycrystalline samples were first washed with absolute alcohol to remove any organic film. They were then degassed at room temperature for at least 12 hours to an ultimate pressure below 10^{-5} mm. Hg. before adsorption measurements were made.

Reduction of the surface oxide which had formed on the nickel powders on exposure to moist air during storage (1), were carried out at 350°C. The hydrogen after thorough drying was passed slowly through the samples at atmospheric pressure. The reduction times are listed in Table 1. Two nickel samples which differed slightly in area but were obtained from the same batch were studied. The first sample was subjected to four reductions. After each reduction the sample was degassed at 25° to 10^{-5} mm. Hg. for 6 hours, then argon adsorption isotherms were determined at -195° . The second sample was studied primarily to substantiate

the results found with the first sample as well as to obtain some additional data for the adsorption of argon at -183° and -195° . After the desired adsorption measurements were made, the samples was again subjected to hydrogen treatment at 350° . Since the reduced nickel was never exposed to any gas except non-reactive helium and argon after the first reduction, the second and subsequent hydrogen treatments were not strictly reductions. Rather they were conducted to allow a study of the change of the surface properties of the metal as sintering progressed; they are labeled reductions merely as a convenience. The hydrogen was used to provide for any accidental contamination of the metal by air during the course of the adsorption measurements.

No effort was made to remove sorbed hydrogen from the reduced samples by degassing at elevated temperatures, since the primary objective of this investigation was to characterize two different surfaces - the oxide-coated and that produced by reduction-by gas adsorption methods. However, to determine the effect of this sorbed hydrogen on the reduced samples on the adsorption of argon, a separate sample was reduced under the usual conditions and degassed at 350° for 3 hours. Large amounts of hydrogen were evolved. Isotherms reduced to unit surface area for this sample and other samples which were reduced but not degassed at high temperature were found to coincide exactly above monolayer coverage indicating that in this region the argon adsorption was independent of any hydrogen presorbed. Beeck (7) also found that the adsorption

(7) O. Beeck, Advances in Catalysis, Academic Press, N.Y.C.
Vol. II (1950) p. 160.

of krypton on nickel films was independent of hydrogen pre-sorbed in his sample.

Procedure - One of the often unrecognized difficulties in adsorption studies at low temperatures is the slow attainment of equilibrium at small adsorption pressures. Spurious rates or heat curves have been shown to result when insufficient time has been allowed for equilibrium (6)(8). To accelerate thermal

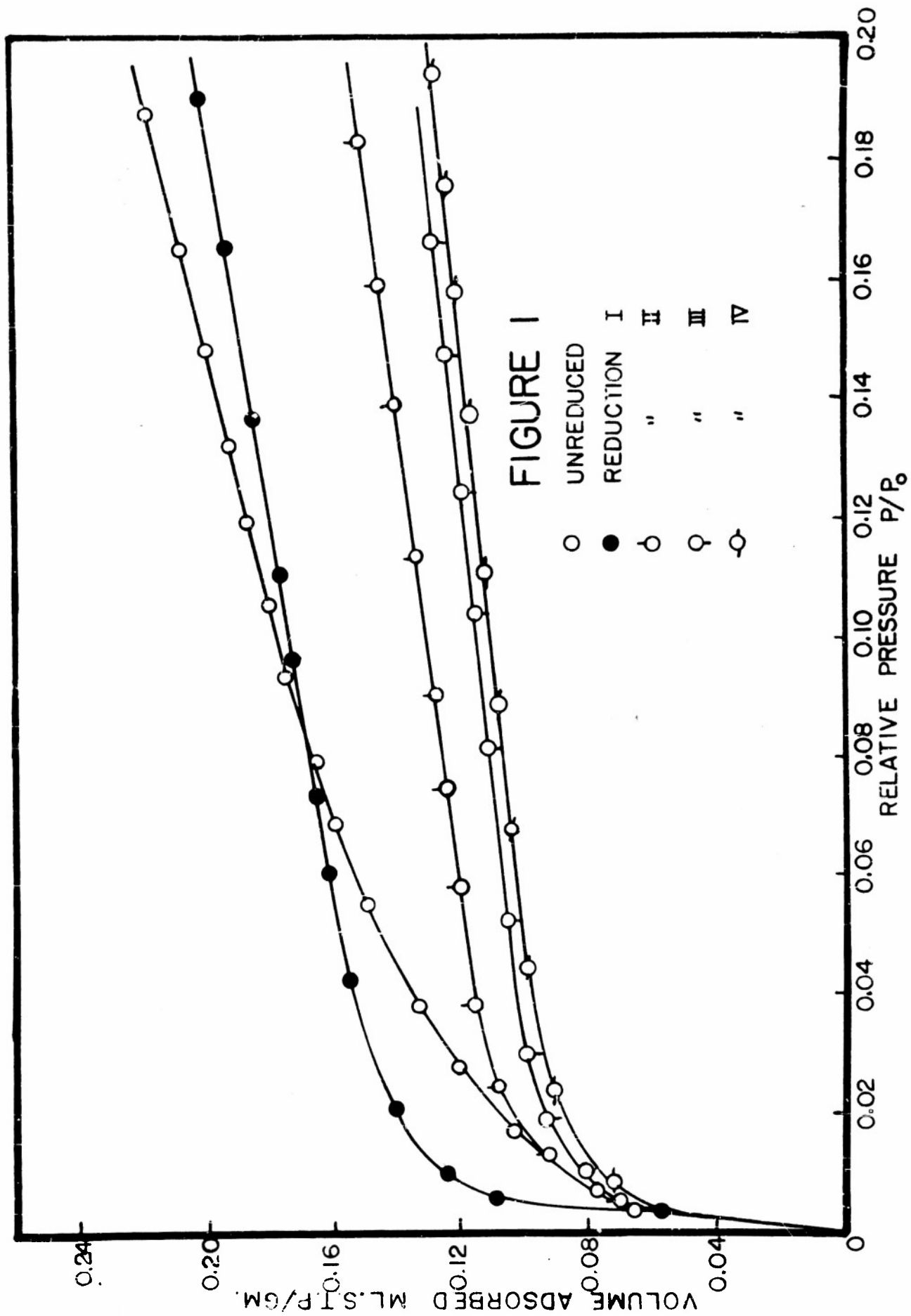
(8) F.C. Tompkin, Trans. Faraday Soc., 34, 1469 (1938).

equilibrium in the low pressure region, it was found expedient to precool the sample in the presence of helium at the adsorption temperature for 2 or 3 hours before adsorption measurements were made. The system was then degassed for 30 minutes at the adsorption temperature and argon adsorption measurements begun. As a result of precooling, equilibrium at pressures below 0.1 mm. was attained within 15 minutes. At high pressures adsorption was complete within 5 minutes.

RESULTS AND DISCUSSION

Adsorption Isotherms - Argon adsorption isotherms measured at -195° on unreduced, oxide-coated nickel and on this sample after each of four successive reductions at 350° are shown plotted in Figure 1. The shapes of the isotherms indicated a marked difference in the behavior of argon adsorbed on the unreduced and reduced powders. Contrariwise, isotherms for argon adsorbed on the reduced nickel samples were found to be very nearly parallel in the region above monolayer coverage although they showed a decrease in the amount adsorbed after each reduction. This decrease, which exponentially approached a limiting value, resulted from a definite increase in particle size of the metal powder due to sintering at the reduction temperature. Confirmation of these initial results was obtained when similar studies were conducted on a new sample of lower initial area but obtained from the same batch of nickel powder. Furthermore, the temperature dependency for adsorption on this second sample was determined at -183° and 195° and isosteric heats of adsorption were calculated.

Some tentative conclusions concerning the natures of the nickel surfaces before and after reduction were possible from a knowledge of the prehistory of the nickel and a visual inspection of these isotherms. First, since the metal was polycrystalline, it was reasonable to assume that the surfaces were heterogeneous. Further, it was concluded that the distributions



of adsorption energy sites on the oxide-coated and reduced metal were quite different. Finally, it appeared that while a new type of surface resulted after reduction of the oxide film, the effect on this new surface of sintering at high temperature was to cause a decrease in area without drastically changing its site energy distribution, particularly at higher coverages. Considerable evidence was obtained to substantiate these findings as well as to yield more quantitative information on the nature of these two different surfaces.

Adsorption Isotherms Reduced to Unit Surface Area -

Adsorption in the first layer, whether chemical or physical, depends on two factors: the extent of the surface and the energy of interaction between surface and adsorbate. Brunauer (9)

(9) S. Brunauer, The Adsorption of Gases and Vapors, Princeton Univ. Press, Princeton, N.J. (1943) p. 329.

designated the former the "non-specific" factor, the latter the "specific" factor in adsorption. This delineation was, of course, an oversimplification since the interactions between adjacent adsorbed molecules can be an important additional factor. However, if physical adsorption were completely "non-specific", then surface area alone would be controlling and isotherms for a gas adsorbed on all types of surfaces would coincide if volumes adsorbed per unit area were plotted against pressure. This situation would not exist, on the other hand, if surface "specificities" were also important. Isotherms of this nature were developed in order to differentiate between the adsorption behavior of argon on both

the unreduced and reduced nickel samples. For this reason a measure of the specific areas of these samples was necessary.

The values for V_m were obtained by the usual BET method and represented the STP volumes of gas required to cover the surface of one gram of sample with one adsorbed layer. The specific areas of the samples were calculated from these V_m values assuming that the adsorbed molecules have the same hexagonal, close-packing as in the liquid state (10). Another method, the

(10) *ibid*, p. 287.

"B" point method of obtaining V_m and corresponding area values, was to use the volume adsorbed at the beginning of the linear portion of the Type II isotherms. This latter method was adopted here because of the better agreement in area values calculated from V_m values at -183° and -195° obtained by this "B" point method. This agreement is shown in the last column of Table I for sample No. 2.

The isotherms measured for the adsorption of argon on unreduced nickel and on this same sample after each of four, successive, high temperature reductions are shown in Figure 2. The adsorption values were reduced to unit area; i.e., V/V_m values were plotted against relative pressure. There was no doubt that the "specific" forces whether surface, adsorbate interaction or both were different for argon adsorbed on unreduced and reduced nickel. On the other hand, the coincidence of the four isotherms for the reduced samples, although they differed in area by as much

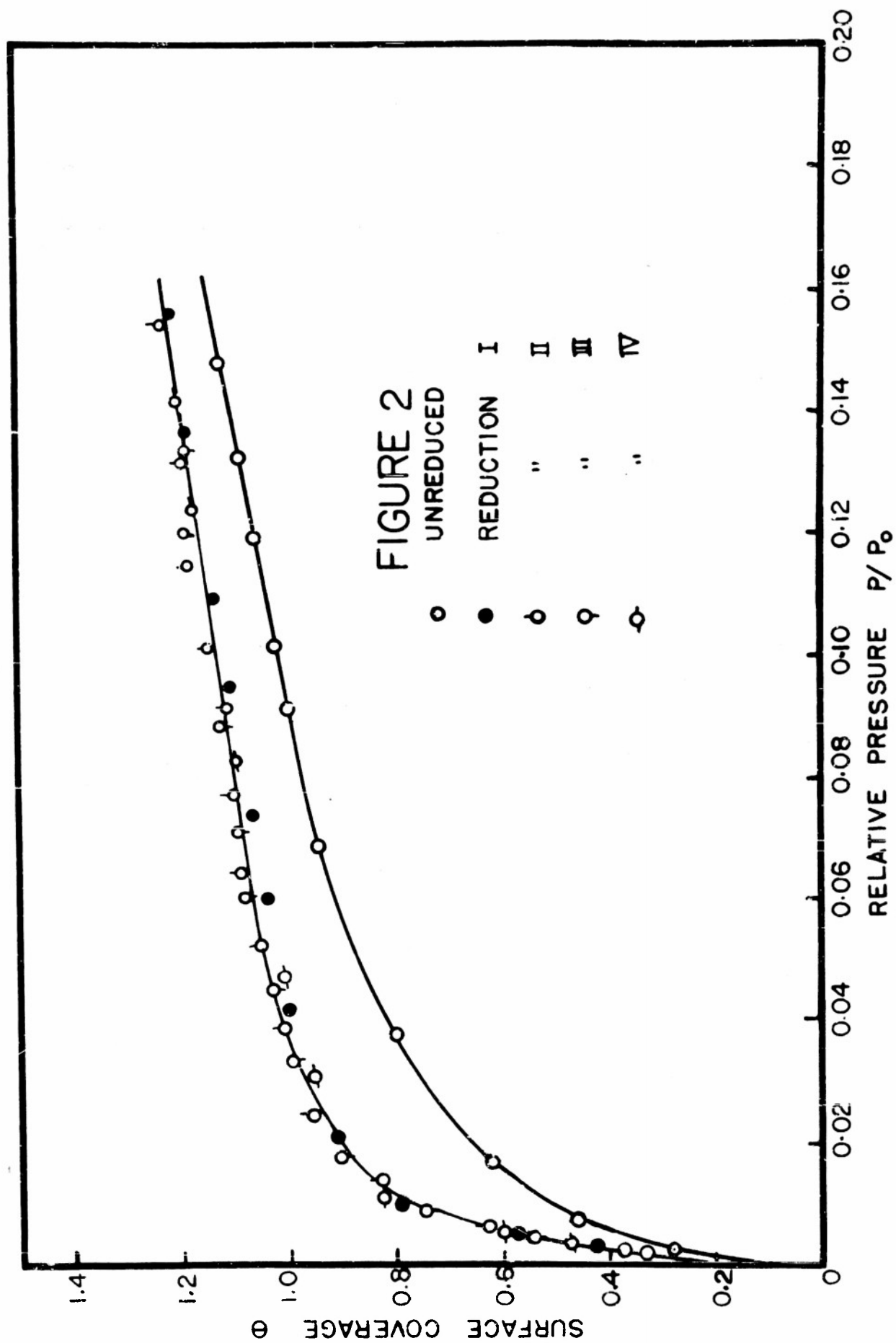


TABLE I
ADSORPTION OF ARGON ON NICKEL

Reduction No.	Time (hrs.)	BET		"B" Point	
		V_m (ml./g.)	Area (m ² /g.)	V_m (ml./g.)	Area (m ² /g.)
Sample #1 -195°C.					
unreduced	-	0.195	0.73	0.167	0.63
1	2.0	0.168	0.63	0.155	0.58
2	3.5	0.119	0.45	0.113	0.43
3	2.5	0.107	0.40	0.103	0.39
4	3.0	0.100	0.38	0.098	0.37
Sample #2 -195°C.					
unreduced	-	0.154	0.57	0.133	0.50
1	2.5	0.117	0.44	0.112	0.42
2	2.0	0.100	0.37	0.098	0.37
-183°C.					
unreduced	-	0.152	0.59	0.126	0.49
1	2.5	0.122	0.47	0.107	0.42
2	2.0	0.104	0.40	0.095	0.37

as 36%, strongly suggested that only small changes in these "specific" forces occurred as a result of sintering at the reduction temperature.

Free Energy Change of Adsorption - Graham (4)

developed a simple distribution function which he claimed provided the basis for a clean cut classification of physical adsorption in terms of the surface properties of the adsorbent as well as adsorbate interaction. The equilibrium constant for the transfer of one mole of adsorbate from the standard state as a liquid to the adsorbed phase can be written:

$$K = \frac{\theta}{(1-\theta)X} \quad (1)$$

where θ is the fraction of surface covered and X is the relative pressure of the gas in equilibrium with solid. The free energy change is simply given by the relationship

$$-\Delta F^0 = RT \ln K \quad (2)$$

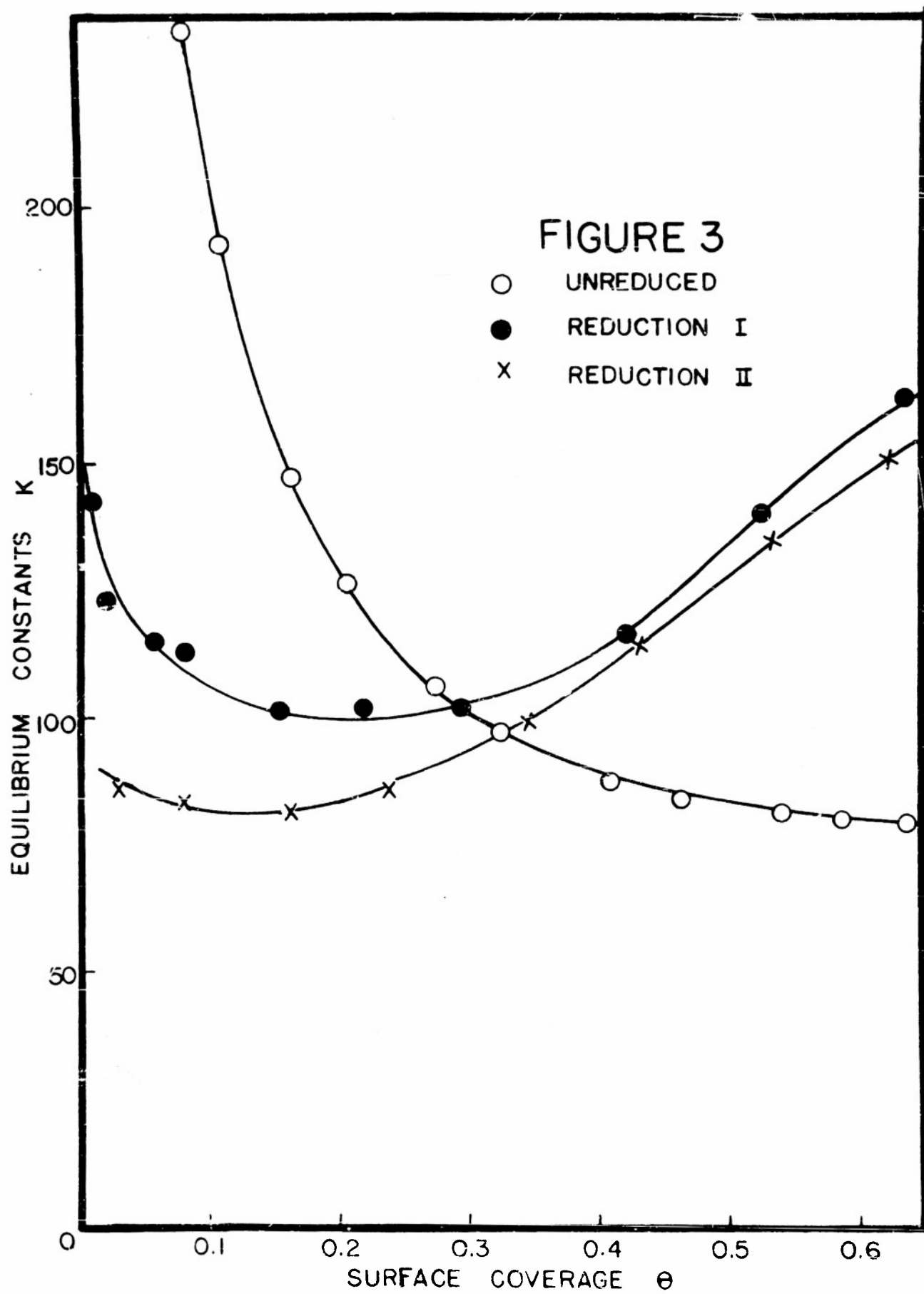
and constitutes a measure of the strength of the adsorption bond. In the ideal case involving localized, non-interacting adsorption on a uniform surface, K is a constant. Therefore, deviations of this constant from ideality can furnish information concerning the factors responsible for non-ideality such as lateral interactions between adsorbed molecules and the heterogeneous nature of the surface.

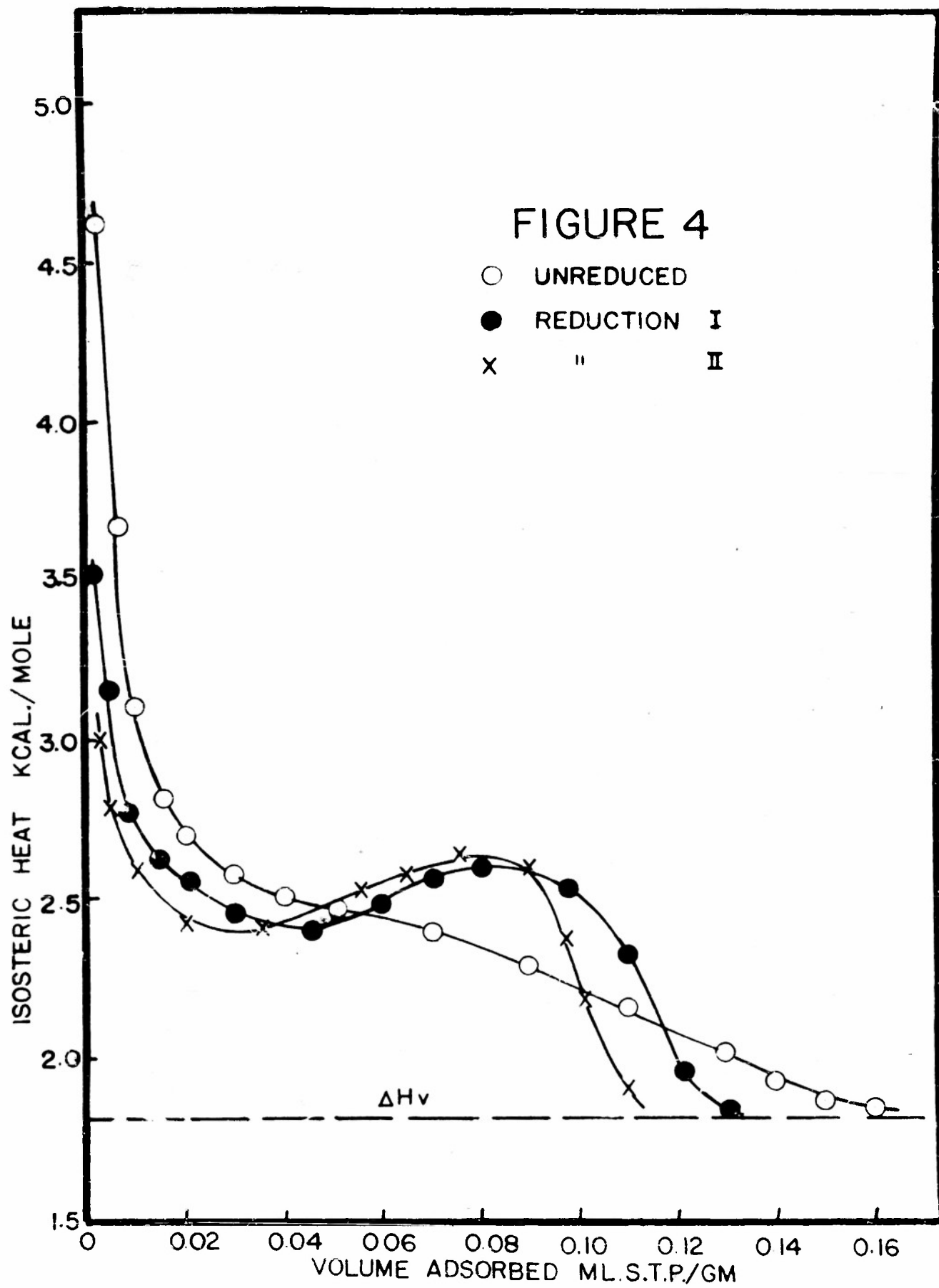
The equilibrium functions for the adsorption of argon on the second sample of the unreduced nickel and for this same sample after each of two successive reductions are shown plotted

in Figure 3 as a function of θ . The shape of the equilibrium function curve for argon adsorbed on the unreduced sample indicated adsorption on a heterogeneous surface. Initial adsorption took place on sites of high energy. Furthermore, these site energies decreased markedly with increasing θ . The equilibrium function was found to be nearly constant between $\theta = 0.5$ to $\theta = 0.8$, the criterion for adsorption on a uniform surface. However, a balance between cooperative adsorption and surface heterogeneity, itself, was probably responsible for the constancy of K in this region.

For the two reduced samples, the values of K were about 25 units apart at $\theta = 0.1$ and became nearly equal as θ increased. This initial difference was evidence for the presence of surface heterogeneities at low coverages which tend to disappear as a result of sintering. Generally, it appeared from the much lower K values that the reduced samples were less heterogeneous than the unreduced nickel. Consequently, interactions between adsorbed molecules and a subsequent increase in K began at very low coverages, ca. $\theta = 0.2$.

Isosteric Heats of Adsorption - Isosteric heat values obtained from adsorption measurements on the second nickel sample are plotted in Figure 4 as a function of the volume adsorbed. The sharp decrease in the heat values at small volumes adsorbed for the unreduced sample was of particular interest. A sharp initial decline in the heat values was found also for the reduced samples but over a smaller range of adsorption. Also, H_0 , the





heat of adsorption at zero coverage was approximately 1.6 kcals. greater for the unreduced sample than for this same sample after one reduction. The rise in the heat curve and subsequent maximum near monolayer coverage was attributable to cooperative adsorption on the reduced surfaces. Almost exact coincidence of the heat curves for argon adsorbed on the reduced samples resulted if these values were plotted as a function of surface coverage θ indicative of adsorption on the same type of surface. However, at low values of θ the heats of adsorption were less after the second reduction. The equilibrium function and isosteric heat data indicated that both the unreduced and reduced nickel samples were heterogeneous and that these surface heterogeneities strongly influenced adsorption in the region of small θ for the reduced samples and to higher values of coverage for the unreduced nickel. Furthermore, the surface heterogeneities on the reduced samples tended to smooth out as a result of sintering at the high temperature employed in the reduction.

Absolute Entropy of the Adsorbed Phase - Hill (2) showed that on a model of localized adsorption on a heterogeneous surface without adsorbate interactions the configurational entropy at temperature T is given by the equation:

$$S_c = k \ln \frac{B_i!}{N_i! (B_i - N_i)!} \quad (3)$$

where B_i represents the sites of energy i and N_i the number of molecules adsorbed on the B_i sites. The maximum possible configurational entropy S_m (T infinite) is expressed by the relation-

ship:

$$S_m = k \ln \frac{B!}{N!(B-N)!} \quad (4)$$

and is independent of the distribution of site energies on the surface. S_m also gives the configurational entropy on a uniform surface. Drain and Morrison (3) carried out the arduous calculations necessary to obtain the configurational entropy from equation 3 as well as the non-configurational entropy for the adsorption of argon on rutile at 85°K. A knowledge of the site energy distribution for argon adsorbed on this solid at 0°K was essential to their calculations and this in turn was obtained from calorimetric measurements of the heat capacities of adsorbed argon films down to very low temperatures. These heat capacity measurements probably represent the only method presently available to obtain a distribution function at 0°K where the surface sites fill strictly in order of their energies.

Since it was impossible to obtain a proper distribution function for the argon-nickel systems studied here, the rigorous calculations of the type outlined by Hill could not be carried out. However, on the basis of the model outlined previously, the integral molar configurational entropy is represented reasonably well by the equation

$$S_c = \frac{\pi^2}{3} \cdot R \cdot \frac{d \ln V}{d \ln p} \quad (5)$$

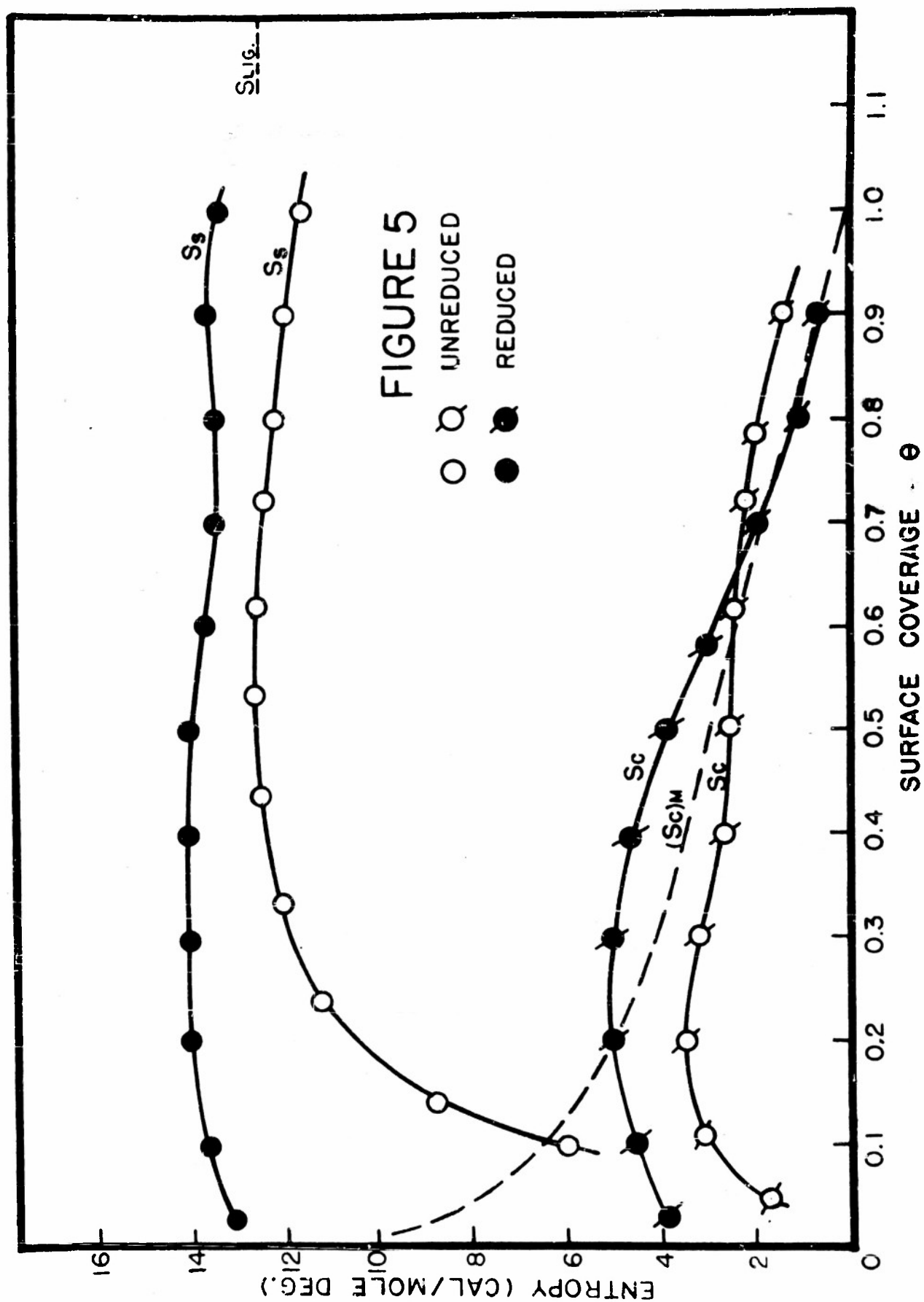
This expression 5 is accurate for a site energy distribution wide compared to RT and should not be in error by more than 20%

even for a homogeneous surface below monolayer coverage (3).

In Figure 5 the experimental molar entropies, S_g , for argon adsorbed on unreduced nickel and this sample after one reduction are plotted as a function of surface coverage, θ . The general shapes of the two curves were similar; i.e., both showed an increase in entropy with increasing adsorption in the range of low θ values and then remained little changed as coverage increased. The absence of high entropy values in the region of small θ was surprising for this adsorbate at this temperature and suggested that adsorption here took place on very heterogeneous portions of the surfaces with small contributions to the total entropy due to configurational effects and particularly so for the unreduced sample.

For localized adsorption on a heterogeneous surface, configurational entropies calculated from equation 5 should be valid for the argon-nickel systems up to the point where interactive adsorption began. Calculated configurational entropy values for both nickel surfaces are compared in Figure 5. These values were one to two entropy units lower for the unreduced surface and supported the contention based on previous data that this unreduced surface was the most heterogeneous of the two types studied. Furthermore, the configurational entropies for both surfaces tended toward zero as $\theta \rightarrow 0$, a fact already deduced from the shapes of the integral entropy curves at low θ .

The calculated, S_c , curves increased with increasing coverage and eventually exceeded the maximum possible configu-



rational entropy, S_m . For the reduced sample, this took place at $\theta \sim 0.2$ and undoubtedly was evidence for the onset of adsorbate interactions at unusually low coverages. The equations developed by Hill (2) to treat adsorption on a heterogeneous surface with nearest neighbor interaction were too complex to treat mathematically even if a proper distribution function were available. Thus it was likely that a model of localized adsorption on a heterogeneous surface without adsorbate interaction was not valid beyond $\theta = 0.2$ and $\theta = 0.5$ for the reduced and unreduced surfaces respectively.

In the presence of interactions a division into a non-configurational and configurational entropy becomes arbitrary. Thus, it becomes difficult to interpret the essentially constant entropy values at higher coverages. These values are very near the entropy of liquid argon for both samples.

Acknowledgment

The authors gratefully acknowledge the financial support provided by the Office of Naval Research, Project NR-057-186, Contract N8onr-74300.

A VOLUMETRIC CALORIMETER FOR
HEATS OF IMMERSION OF SOLIDS
INTO LIQUID NITROGEN

INTRODUCTION

Immersional calorimetry for the study of systems at or near room temperatures has been well developed (1,2,3),

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- (1) G.E. Boyd and W.D. Harkins, J. Am. Chem. Soc., 64, 1190 (1942)
 - (2) E. Hutchinson, Trans. Faraday Soc., 43, 443 (1947)
 - (3) A.C. Zettlemoyer, G.J. Young, J.J. Chessick, and F.H. Healey, J. Phys. Chem., 57, 649 (1953)
-

and has lead to valuable data concerning the interaction between surface and adsorbate supplemental to that obtained from gas adsorption studies. To obtain such information from the immersion of a solid in a liquid whose normal temperature is far removed from room temperature special procedures are required to detect the minute temperature changes resulting from the wetting of a solid by the liquid.

A simple and accurate method has been developed for the measurement of the heats of immersion of solids in liquid nitrogen at its boiling point at -195° . This technique, the measuring of the volume of liquid vaporized, requires none of the elaborate and expensive equipment usually used in immersional calorimetry and, in addition, can be applied to the immersion of solids in other liquids at their boiling points.

EXPERIMENTAL

Low Temperature Immersional Calorimeter: The low temperature calorimeter is shown in Figure 1. Heat effects are measured by the amount of liquid nitrogen which is vaporized and collected as a gas when a clean sample is broken under the liquid. The calorimeter consists of two sections of a large glass tube joined by means of a 45/50 standard taper joint. A hollow tube, A, with a shield, B, to prevent spattering of liquid nitrogen is sealed to the upper calorimeter section. The breaker rod, C, passes through this tube and rests on top of the sample tube, D. A tight fitting piece of rubber tubing is used to form an air tight seal between this tube and the breaker rod; the tubing allows sufficient movement of the rod to break the sample tube. The exit tube, E, is connected to a gas burette by means of rubber tubing. The calorimeter is immersed in a large Dewar flask containing liquid nitrogen. Liquid nitrogen is introduced into the calorimeter, itself, through tube, E.

Sample Tube Breaking: The sample tubes are specially constructed so that the bottoms have very thin walls. The tubes rest on a formed rubber support with the breaker rod immediately above the thin wall portion. A light tap of the breaker rod is sufficient to pierce the sample tube. Blank runs indicate that the heat effect resulting from breaking in this manner is so small that it contributes only from 5 to 15 ml. to the total amount of gas evolved. A cor-

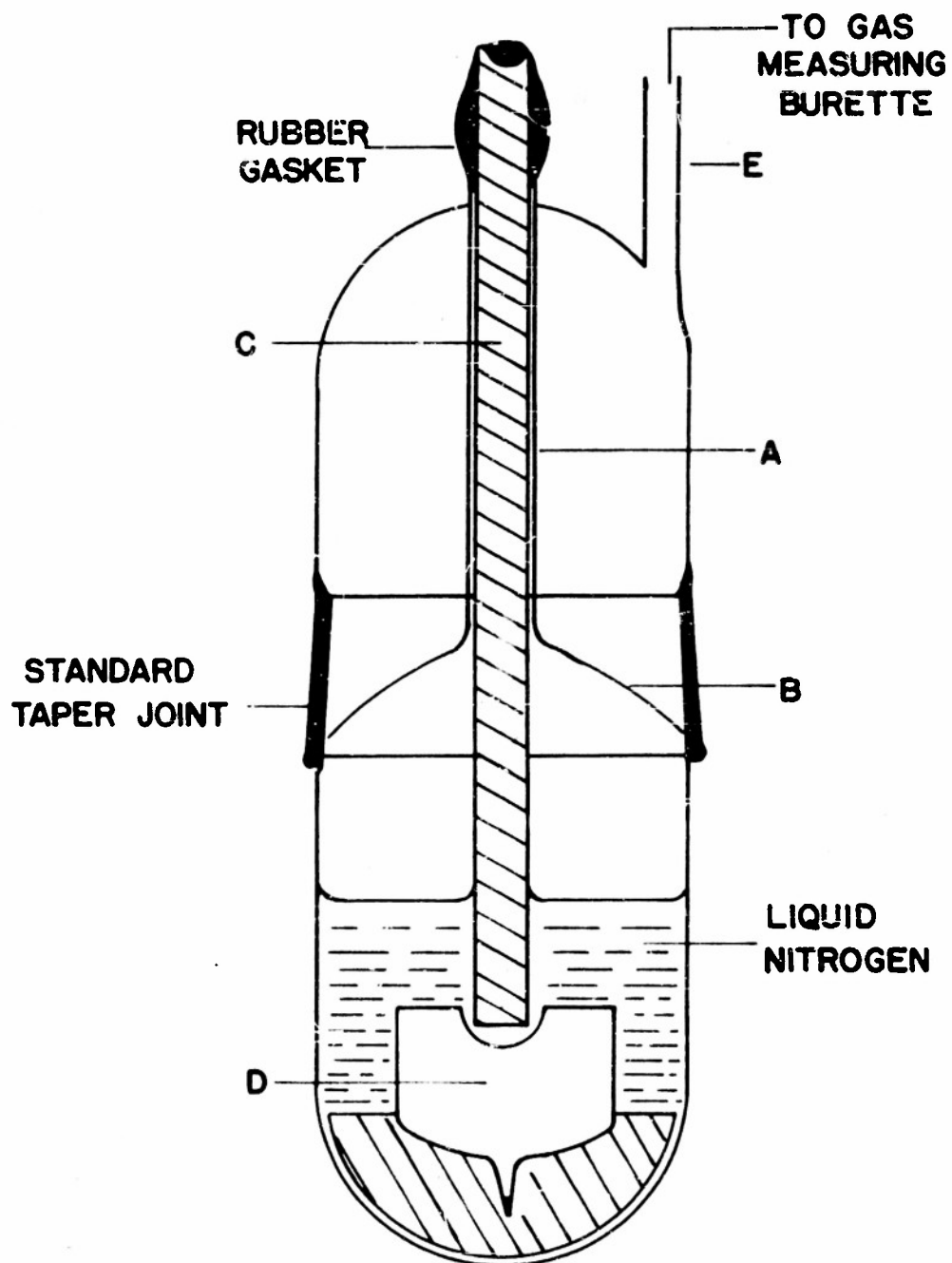


FIGURE 9

LIQUID NITROGEN IMMERSION CALORIMETER

rection of 10 ml. was applied to all measurements.

Rating Periods: Once temperature equilibrium between the calorimeter and bath is reached the amount of nitrogen gas evolved each minute is determined by displacement of water from a gas burette. The amount of gas evolved was found to be constant for periods of 0.5 to 1.0 hours, and is a function of the purity of liquid nitrogen used and the barometric pressure; the most pronounced influence, however, is that produced by the latter. The rates varied from 20 to 50 ml. of gas evolved per minute using commercial liquid nitrogen with measured vapor pressures between 79 and 82 cm. Hg. No runs were made using a particular liquid nitrogen supply if the rating period exceeded 50 ml. per minute.

Procedure: For the results described below, samples weighing 4 to 10 grams were evacuated under the conditions listed in Table I, then were sealed off under vacuum and transferred to the calorimeter. Before joining the two sections of the calorimeter, Apiezon "M" grease was applied to the standard taper joint. The entire calorimeter was placed in a large Dewar flask and liquid nitrogen was added to the flask until the liquid level was about one-inch above the top of the calorimeter. After a few minutes 250 ml. of liquid nitrogen was added to the calorimeter, itself, through the exit tube. Rubber tubing leading to the gas burette was then attached to the exit tube and the displacement of water

by the nitrogen gas evolved was noted. The maximum time for temperature equilibrium between the calorimeter and bath to be reached was three hours. A time-gas volume curve was followed until a steady rate of gas evolved was obtained over a ten minute period. The sample was broken under the liquid and the time noted. Time-volume readings were continued for 10-15 minutes after breaking. The heat of immersion was always evolved within less than one minute after breaking. The smallest volume of gas evolved was about 100 ml. (STP); the average volume was about 200 ml.

The gas evolved as a result of the wetting process was corrected for the height of the column of water in the gas burette, as well as for the presence of water vapor, then converted into ml. evolved at STP. The heat of immersion in ergs/cm². was calculated from the formula:

$$h'_{(SL)} = - \frac{\Delta V(\text{ml. STP})}{22,400} \left| \frac{1333}{\text{wt.}} \right| \frac{4.187 \times 10^7}{\text{area cm}^2/\text{g.}}$$

where 1333 cal./mole is the heat of vaporization of liquid nitrogen.

Adsorption Measurements: Isotherm data at 77.8 and 72.3°K for the adsorption of nitrogen on magnesia "2642" were selected from the results of a study previously conducted in this laboratory; a detailed discussion of these earlier experimental techniques has been fully described (4).

(4) A. C. Zetlemoyer and W. C. Walker, Ind. and Eng. Chem., 39, 69 (1947).

Experimental Results and Reproducibility: Values of the heats of immersion for a variety of solids from liquid nitrogen are tabulated in Table I. The average deviation represents a measure of the reproducibility of the results. The maximum deviation amounts to about 5% which is good agreement because a combination of factors such as weighing, pretreatment, activation and evacuation of the samples as well as direct calorimetric measurements affect these values.

TABLE I
Heat of Immersion of Solids in Liquid Nitrogen at -195°

Sample	Specific Area $\text{m}^2/\text{g.}$	Heat of Immersion ergs/cm^2	Number of Determinations	Activation Time hrs.	Temp. $^{\circ}\text{C.}$
Graphon (a)	83.0	-104 ± 1	3	24	25
Silene (EF) (b)	51.6	-102 ± 1	3	24	25
Alumina (F10) (c)	119.2	-104 ± 5	4	2	400
Magnesia "2642" (d)	112.7	-105 ± 4	4	1	250

- (a) Lot L-2739, Godfrey L. Cabot Co., Boston, Mass; a graphitized carbon black: the maximum amount of surface oxide has been estimated to occupy no more than 1/1500 of the total area. "Thermodynamics of the Adsorption of Water on Graphon", G.J. Young, J.J. Chessick, F.H. Healey and A.C. Zettlemoyer, to be published J. Phy. Chem. about May 1954.
- (b) Ppt. Calcium Silicate, Pittsburg Plate Glass Co., Pittsburg, Pa.
- (c) Lot 202, 8-14 mesh, Aluminum Co. of America, Pittsburg, Pa.
- (d) Furnished by Westvaco Chemicals Division, Food Machinery Corporation.

An important observation is the fact that the values of the heats of emersion are practically the same for these four different solids. Since the surfaces of these solids are considerably different, especially the hydrophobic Graphon, this finding suggests that the volume of gas evolved when one gram of a clean solid is immersed in liquid nitrogen may be taken as a measure of the specific area.

DISCUSSION

When a nonporous solid is immersed in a liquid, the solid surface with its energy disappears and is replaced by a solid-liquid interface. The heat of emersion (5) for the

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- (5) Because of the convention established by W.D. Harkins, the heat of emersion will be discussed in the theoretical section of this paper. Furthermore, the definition of the spreading pressure $\phi = \gamma_s - \gamma_{sl}$ has been conventionally established for the desorption process.
-

process is given by the relationship:

$$h_{SL} = \left[\gamma_s - \gamma_{SL} - T \left(\frac{\partial \gamma_s}{\partial T} - \frac{\partial \gamma_{SL}}{\partial T} \right) \right]_{P, \Sigma} \quad (1)$$

where γ_s and γ_{SL} are the free surface energies of the clean solid and the solid-liquid interface at temperature T , and Σ is the surface area of the solid. The value of h_{SL} for the emersion of MgO from liquid nitrogen at -195° was obtained experimentally and compared to values calculated by two methods using adsorption data. It was pertinent to inquire, also, into the relative importance of the contributions to the heat of

emersion for this process by both the free energy and entropy terms.

Calculated Heat of Emersion from Isosteric Heats of Adsorption: The difference in the internal energy, E_L , of a liquid adsorbate in equilibrium with vapor at T , and the energy, E_a , of the adsorbate molecules is given by the relationship (6)

(6) G. Jura and T.L. Hill, J. Am. Chem. Soc., 74, 1498 (1952).

$$E_L - E_a = (h_{sL} - h_{sfL}) / N_a \quad (2)$$

where h_{sL} and h_{sfL} are the heats of emersion of a clean solid and a solid with N_a adsorbed molecules. The term is related to the isosteric heat, q_{ST} , by an equation readily obtained from Equation 91 of Hill (6)

(6) T.L. Hill, J. Chem. Phys., 17, 520 (1949)

$$h_{sL} - h_{sfL} = \int_0^{N_a} q_{st} dN_a - N_a \Delta H_v \quad (3)$$

where ΔH_v is the molar heat of vaporization of nitrogen. The term $h_{sL} - h_{sfL}$ can thus be obtained by graphical integration of a q_{ST} vs. N_a plot.

The heat of immersion of a solid, which has been exposed to the saturated vapor of the liquid until the adsorbed film attains equilibrium with respect to the vapor, is given by the equation (7):

- (7) W.S. Harkins, "The Physical Chemistry of Surface Films", New York, Reinhold Publishing Co., 1952, pg. 274.

$$h'_{sL} = - \left[\left(\gamma_L - T \frac{\partial \gamma_L}{\partial T} \right) \cos \theta + T \gamma_L \sin \theta \frac{\partial \theta}{\partial T} \right] \quad (4)$$

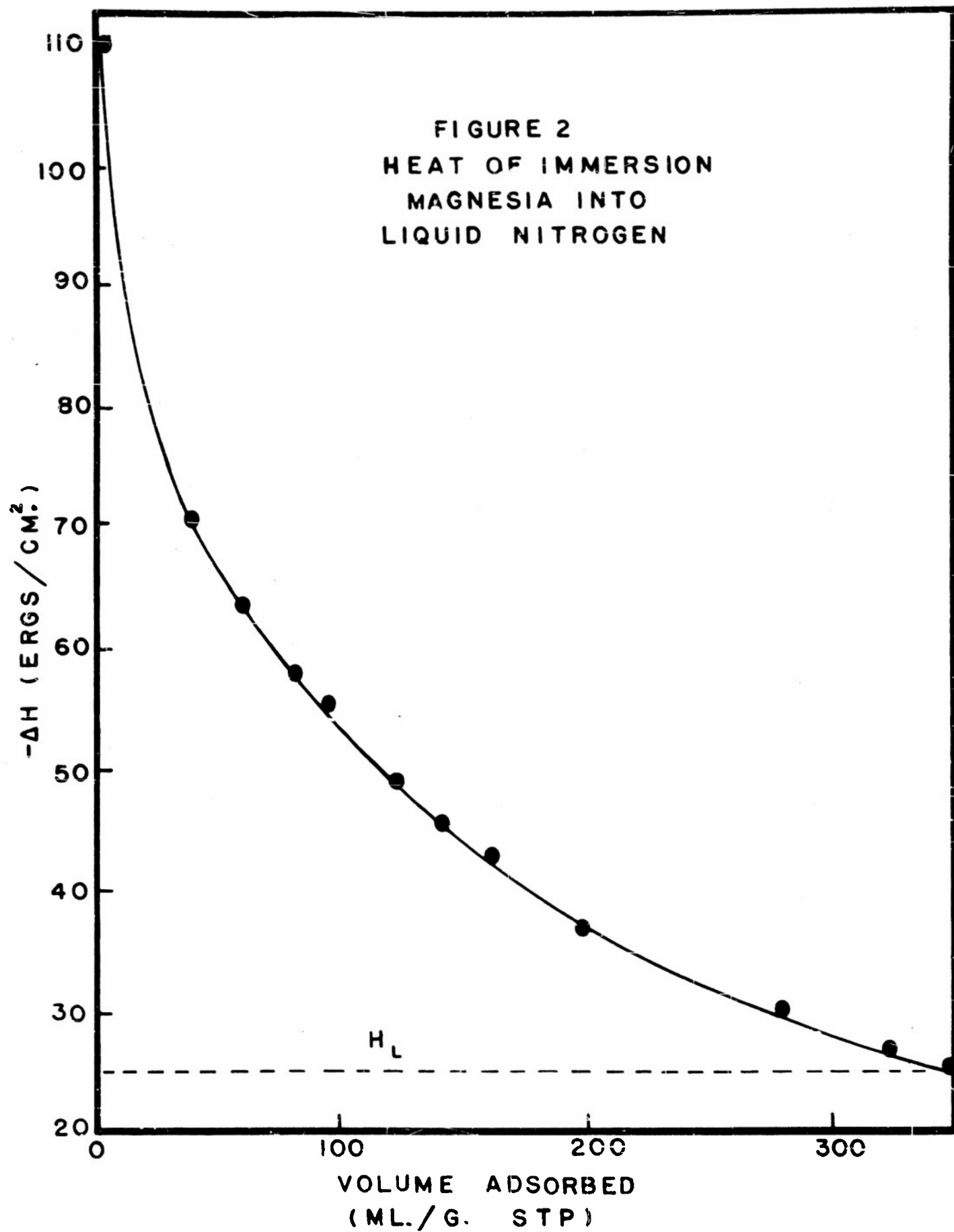
where γ_L is the free surface energy of the liquid and θ is the contact angle of the liquid on the surface. If $\theta = 0$, then the heat of emersion is

$$h_{sEL} = \left[\gamma_L - T \left(\frac{\partial \gamma_L}{\partial T} \right) \right] = h_L \quad (5)$$

Equation (5) represents the heat content of the surface of the liquid used. The value of this quantity for liquid nitrogen (25.2 ergs/cm² at 74.9°K) was obtained from the surface tension and temperature variation of the surface tension of the liquid. The heat of emersion, h_{sL} , of clean MgO was calculated to be 110 ergs/cm² from a knowledge of h_L and the differences in the heats of emersion at saturation obtained from equation (3). This value compares with the value of 105 ergs/cm² found experimentally.

The calculated values for the heat of emersion of MgO are shown plotted in Figure 2 as a function of the volume of nitrogen adsorbed. The heat values approach the value for the heat content of a liquid nitrogen surface only at high surface coverage, ca. 10 molecular layers (8).

FIGURE 2
HEAT OF IMMERSION
MAGNESIA INTO
LIQUID NITROGEN



- (8) In contrast, heat values for the emersion of asbestos from water approach the surface enthalpy of liquid water very nearly after the completion of a monomolecular layer (3).

Calculated Heat of Emersion from Absolute Entropy Values:

The equilibrium heats of adsorption, $H_G - H_a$ and the corresponding integral entropy values, $S_G - S_a$ where the subscript, G, refers to gaseous nitrogen in equilibrium with the adsorbed film, a, were calculated for the adsorption of nitrogen on MgO (9).

- (9) T.L. Hill, J. of Chem. Phys., 17, 520 (1949)

The equilibrium heats were obtained from the Clausius-Clapeyron equation at constant spreading pressure, φ . Thus it was necessary to determine φ as a function of the equilibrium pressures at two temperatures from adsorption data by graphical integration of the Gibbs equation:

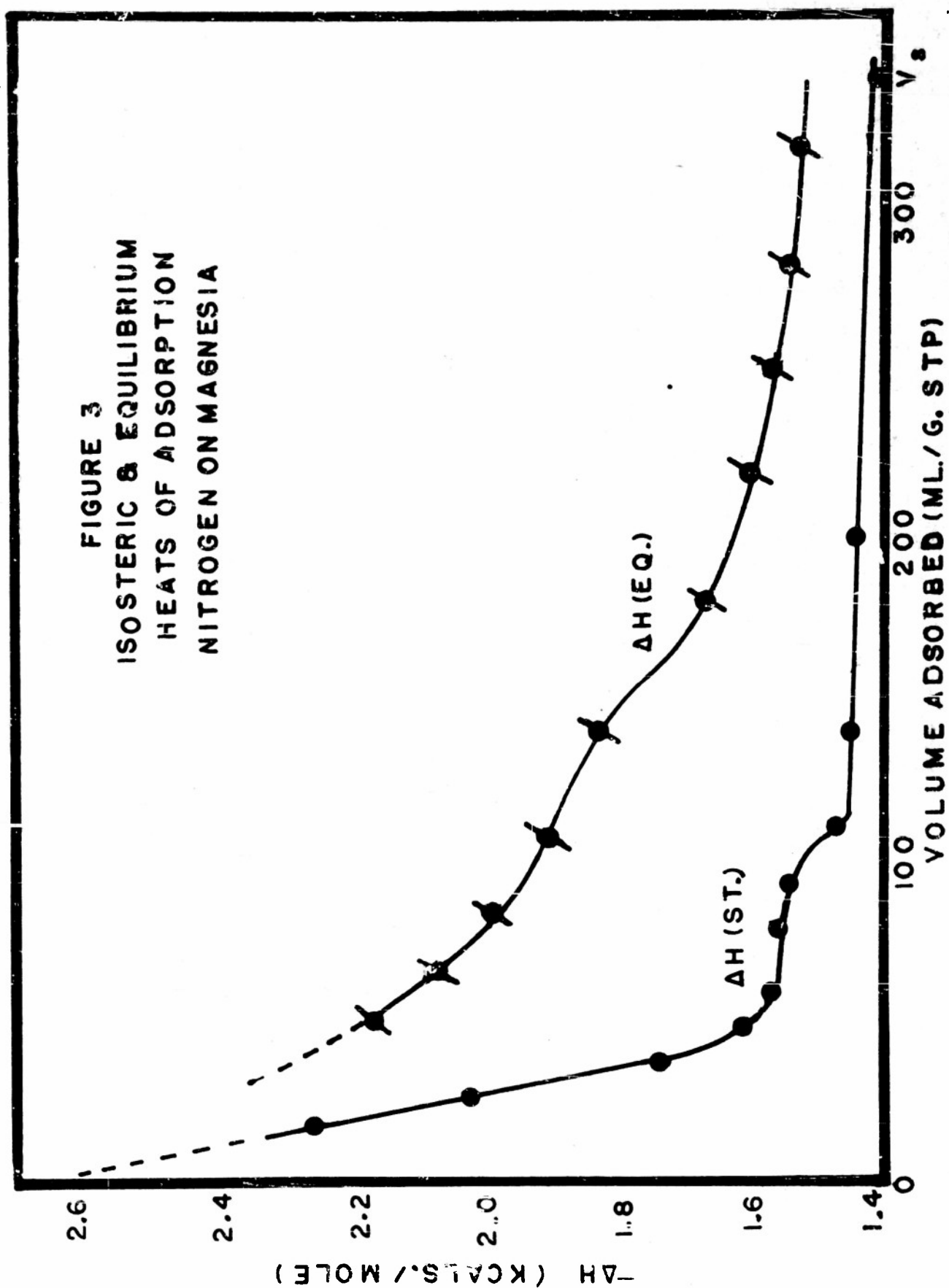
$$\varphi = \gamma_s - \gamma_{sf} = kT \int_0^{\bar{n}} \bar{n} d \ln p \quad (6)$$

where $\bar{n}$ is the surface concentration. The equilibrium and isosteric heats of adsorption are plotted in Figure 2 as a function of the volume adsorbed.

When the contact angle of a liquid on a solid is zero, and, further, if the film formed on a solid in equilibrium with the saturated vapor of the liquid is duplex then

$$\gamma_{se} = \gamma_{sl} + \gamma_L \quad (7)$$

FIGURE 3
ISOSTERIC & EQUILIBRIUM
HEATS OF ADSORPTION
NITROGEN ON MAGNESIA



and equation (1) can be written in the form

$$h_{SL} = \left[\phi_e + \gamma_L - T \left(\frac{\partial \phi_e}{\partial T} \right) - T \left(\frac{\partial \gamma_L}{\partial T} \right) \right] \quad (8)$$

The temperature coefficient, $\partial \phi_e / \partial T$, of the difference in the free surface energy of a clean solid and a film covered solid is related to the difference in the integral entropy term

$$\partial \phi_e / \partial T = -N_a k \ln X + N_a (S_a - S_L) \quad (9)$$

At saturation the relative pressure, X , of the gas in equilibrium with the adsorbed film is equal to unity, thus

$$\partial \phi_e / \partial T = N_a (S_a - S_L) \quad (10)$$

The term $(S_a - S_L)$ was obtained from the equilibrium heat of adsorption at saturation and a knowledge of the entropy of vaporization of liquid nitrogen at 74.9° K.

Table II contains values for measured and calculated quantities used to obtain the heat of emersion of magnesia from liquid nitrogen. A value of 117 ergs/cm². was calculated from equation 8. The $\partial \phi_e / \partial T$ term was obtained from entropy data (eqn. 10). This value of 117 agrees fairly well with the value of 110 ergs/cm². obtained from isosteric heat data (eqn. 3) as well as with the experimental value of 105 ergs/cm². It is also evident from Table II that the $T\Delta S$ term contributes most to the heat term, that is about three times more than the free energy contribution.

Acknowledgment: The authors gratefully acknowledge the financial support provided by the Office of Naval Research, Project NR 057-186, Contract N8onr - 74300.

TABLE II
Free Energy and Entropy Values

Terms	Values ergs/cm ² deg.		
$\partial(\gamma_s - \gamma_{se})/\partial T$	-0.92 ^(a)		
$\partial(\gamma_s - \gamma_{sl})/\partial T$	-1.22		
		ergs/cm ²	
γ_L	9.39		
$\partial\gamma_L/\partial T$	-0.22		
γ_e	22.3		
$h_{sl} - h_{seL}$		85.0	
h_{seL}		25.2	
$\Delta F = \gamma_s - \gamma_{sl}$	31.7		
$T\Delta S = T[\partial(\gamma_s - \gamma_{sl})/\partial T]$	85.5		
ρ_{sl}	117.0 ^(b)	110.0 ^(c)	105 $\pm$ 4 exp.

(a) from eqn. 10.

(b) from eqn. 8, based on entropy values.

(c) from eqn. 3, based on isosteric heat values.

THE DETECTION OF HYDROPHILIC HETEROGENEITIES
ON A CARBON SURFACE

INTRODUCTION

The purpose of this investigation was to study the effect of surface heterogeneity on the adsorption of water on a hydrophobic surface. The system Graphon-water was chosen because Graphon possesses a well-defined hydrophobic and almost homogeneous surface with a very small fraction of hydrophilic heterogeneities (1,2) which are responsible for

-
- (1) Pierce and R.N. Smith, J. Phys. and Colloid Chem. 54, 784 (1950).
(2) G.J. Young, J.J. Chessick, F.H. Healey, and A.C. Zettlemoyer, J. Phys. Chem. 58, 313 (1954).
-

the adsorption of water at low pressures. It appeared possible to increase the fraction of hydrophilic sites by controlled oxidation of the Graphon and to observe the changes produced in the water adsorption isotherm and the heat of immersion in water. It was of interest to determine the relation between the heat of immersion and the fraction of surface which was hydrophilic.

The application of the BET equation to the adsorption of water on Graphon has been shown to give values consistent with the thermodynamic criteria of a complete monolayer (2). Unpublished work in this laboratory with known mixtures of a hydrophilic surface, rutile, and a hydrophobic surface, Graphon, has demon-

strated that the ratio of the apparent surface area determined by water adsorption to the total area determined by nitrogen adsorption is a direct measure of the fraction of hydrophilic surface present in the mixture. Accordingly this ratio has been used in the present work to characterize the hydrophilic heterogeneity of the Graphon surface before and after oxidation.

EXPERIMENTAL

Materials and Apparatus - The Graphon sample was from the same lot, No. 2808, as used previously (2) and was supplied by Godfrey L. Cabot, Inc. The area determined by nitrogen adsorption was 98 m.²/g., and the freshly prepared sample was reported to contain 0.25% ash and 0.2% volatile matter. The samples were not treated with hydrogen since it was desired to preserve any heterogeneous surface sites.

High purity nitrogen, helium, oxygen and water were used and further purified by procedures previously described (3).

(3) A.C. Zettlemoyer and J.J. Chessick, J. Phys. Chem., **58**, 242 (1954).

Nitrogen adsorption and static oxidation studies were made with a BET type adsorption apparatus; water vapor adsorption measurements and procedures using a modified Orr apparatus have been described (2).

Dynamic Oxidation - Tank oxygen at 1 atmosphere without further purification was passed slowly through the samples

at 530° for various time periods (listed in Table I). The Graphon sample was then cooled to room temperature and degassed at 10^{-5} mm. Hg. A portion of the sample was used for adsorption measurements and the remainder subjected to further oxidation under the same conditions.

Static Oxidation - The samples were degassed at room temperature for 12 hours before oxidation. Moist oxygen, made by mixing known volumes of water vapor and dry oxygen to obtain a relative humidity of ca. 0.5, was admitted to the sample at room temperature and the equilibrium pressure recorded. The sample was then heated to 530° within a time interval of ten minutes. The total pressure at this temperature was approximately one atmosphere. The temperature was controlled to $\pm 5^\circ$ throughout the oxidation and any changes in pressure were noted. After two hours the sample was cooled to room temperature and the final equilibrium pressure was recorded.

Adsorption Measurements - About 0.5 grams of Graphon was used for nitrogen surface area determinations at -195°. The surface areas were calculated by the BET method using a close-packed adsorbate area of $16.2 \text{ \AA}^2$. Water vapor adsorption measurements were made at 25° with 5 to 0.5 gram samples depending on the extent of oxidation of the surface. An experimental deviation of 0.005 ml. adsorbed was observed at the lower pressures.

With one sample the weight change caused by successive oxidations was followed. After each oxidation water vapor was

admitted to a relative pressure of 0.3, at which pressure, as determined by the volumetric measurements, the BET V_m value was reached. The amount of water adsorbed was then measured gravimetrically with a correction made for the vapor in the dead space. The results agreed with the volumetric measurements within experimental error.

Heat of Immersion Measurements - The calorimeter and procedure have been described earlier (4). Heats of

(4) A.C. Zetlemoyer, G.J. Young, J.J. Chessick and F.H. Healey, J. Phys. Chem., 57, 649 (1953).

immersion in water were measured for Graphon after the various types of treatment given below.

Treatment of Samples - Sample A was oxidized by the dynamic process. Sample B received the static oxidation treatment with nitrogen and water vapor adsorption determined volumetrically. A second sample treated and measured in the same way checked the results obtained with Sample B. Sample C was activated at 900° for two hours with continuous pumping to study the thermal decomposition of the heterogeneous surface sites present on the original sample. Sample D received the same oxidation treatment as sample B but weight losses on oxidation and water adsorption measurements were made gravimetrically.

When this work was initiated it was hoped that the number of surface oxide sites formed could be directly measured from the oxidation data. However the complexity of the oxidation

process (5) and particularly when water was present (6) pre-

(5) E.A. Gulbransen, Ind. Eng. Chem., 44, 1045 (1952).

(6) R. Smith, C. Pierce, and C.D. Joel, J. Phys. Chem. 58, 298 (1954).

vented any direct determination of the amount and nature of the surface oxide formed. A further complication was introduced when it was found the O₂, CO, and particularly CO₂ all showed some physical adsorption on Graphon at room temperature. The isotherms were linear and at 20 mm. Hg. pressure the respective volumes adsorbed were 0.0055, 0.0090 and 0.029 ml./g.

RESULTS AND DISCUSSION

The apparent surface areas determined by application of the BET equation to the adsorption isotherms of water vapor and nitrogen on Sample A after various times of dynamic oxidation are given in Table I. The apparent area available to water vapor adsorption increased, as was expected, with increasing time of oxidation. The nitrogen or "true" surface area also increased markedly, the final area of 181 m.²/g. being roughly double the original value. The ratio of the apparent water area to the nitrogen area can be considered to be a measure of the surface heterogeneity, i.e., the fraction of hydrophilic sites present on the surface. The ratio may also be considered to be a measure of hydrophobicity; the smaller the ratio, the more hydrophobic the surface. The original sample had a surface with only about

TABLE I
Dynamic Oxidation at 530° - Sample A

Total Time of Oxidation (hrs.)	Apparent Σ H ₂ O	BET Area (m. ² /g.) Σ N ₂	$\frac{\Sigma \text{H}_2\text{O}}{\Sigma \text{N}_2} \times 10^2$
0	0.26	93.0	0.27
2	1.06	110.3	0.96
3	2.05	114.2	1.80
5	3.52	135.7	2.24
10	12.45	152.0	8.20
17	22.52	180.9	12.44

1/400 of the surface hydrophilic; after 17 hours of oxidation about 1/8 of the surface had become hydrophilic. In other words about one-eighth of the surface had been oxidized by this treatment. At the same time a considerable portion of the sample was lost; the sample weight used in the last oxidation 0.42 g. and after 7 hours this weight had been reduced to 0.09 g.

The oxidations carried out in a static, moist, oxygen atmosphere were much less drastic in their effect on the sample as shown in Table II. The nitrogen surface area increased by only 5% after 12 hours of oxidation compared to an increase of over 50% after ten hours of dynamic oxidation. Further, at this point only about 1/70 of the surface had been oxidized.

The sample activated at 900° showed only a slight increase in the nitrogen surface area and a marked decrease in

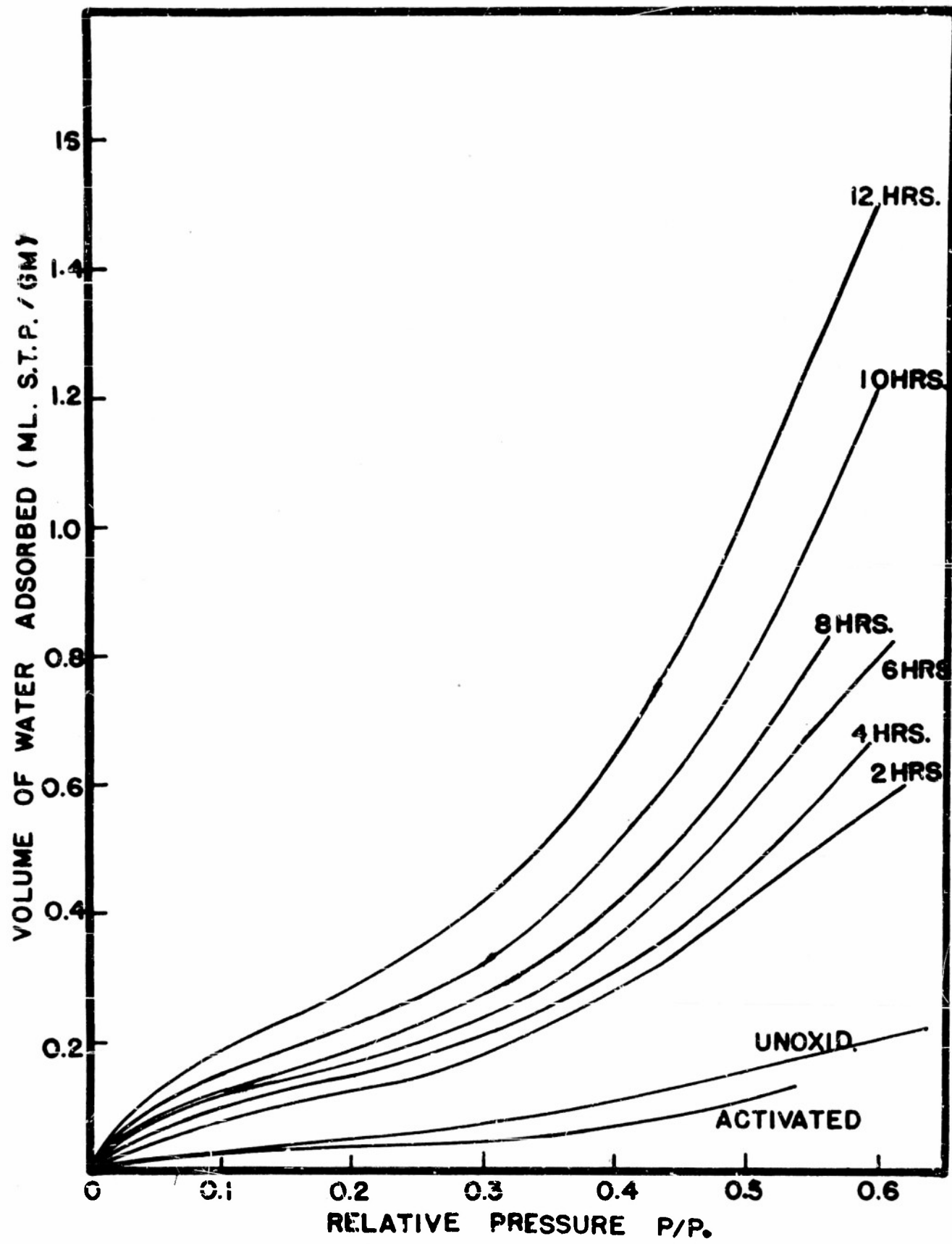
TABLE II
Static Oxidation - Sample B

Total Time of Oxidation (hrs.)	Apparent BET Area (m. ² /g.) $\sum \text{H}_2\text{O}$	$\sum \text{N}_2$	$\frac{\sum \text{H}_2\text{O}}{\sum \text{N}_2} \times 10^2$
0	0.26	98	0.27
2	0.50	101	0.50
4	0.64	103	0.62
6	0.85	102	0.83
8	0.96	102	0.94
10	1.16	103	1.13
12	1.44	102	1.41
Sample C Activated, 9000°, 2 hrs.	0.15	100	0.15

the number of hydrophilic sites, presumably due to volatilization of carbon-oxygen surface complexes. About 45% of the hydrophilic sites were destroyed by activation.

To demonstrate the effect of increasing the percentage of hydrophilic heterogeneity on the adsorption of water, the isotherms at 22° after the various static oxidation treatments are shown on the next page. It is evident that the successive oxidations caused a continual increase in the volume of water adsorbed at all relative pressures. The adsorption isotherm reported by Pierce and Smith (7) for water on Graphon which had

(7) C. Pierce and R.N. Smith, J. Phys. and Colloid Chem. 54, 795 (1950).



been treated with hydrogen at 1100° would lie slightly above the curve for the original (unoxidized) sample. Since their sample had a nitrogen surface area about 20% less than the present Graphon, their surface must have still contained after treatment a considerable amount of hydrophilic heterogeneities. Recently it was reported (6) that the earlier Graphon contained considerable more sulfur than more recent samples and this may be the cause of the greater water up-take.

The increase in the fraction of hydrophilic sites appeared to increase approximately linearly with time of oxidation although there was considerable scatter due in part perhaps to the uncertainty in choosing the best straight line in the BET plots used to obtain ΣH_2O . The rate of apparent surface oxidation, assuming one molecule of H_2O adsorbed per oxide site at V_m , was $0.0019 \pm .0005$ surface sites per hour. With Sample D where the static oxidation was carried to 20 hours and the water pick-up determined gravimetrically the curve was shown to be actually parabolic, and that furthermore, the sample showed a considerable loss in weight. The rate of increase in the fraction of hydrophilic sites cannot, therefore be taken as a measure of the rate of total oxidation.

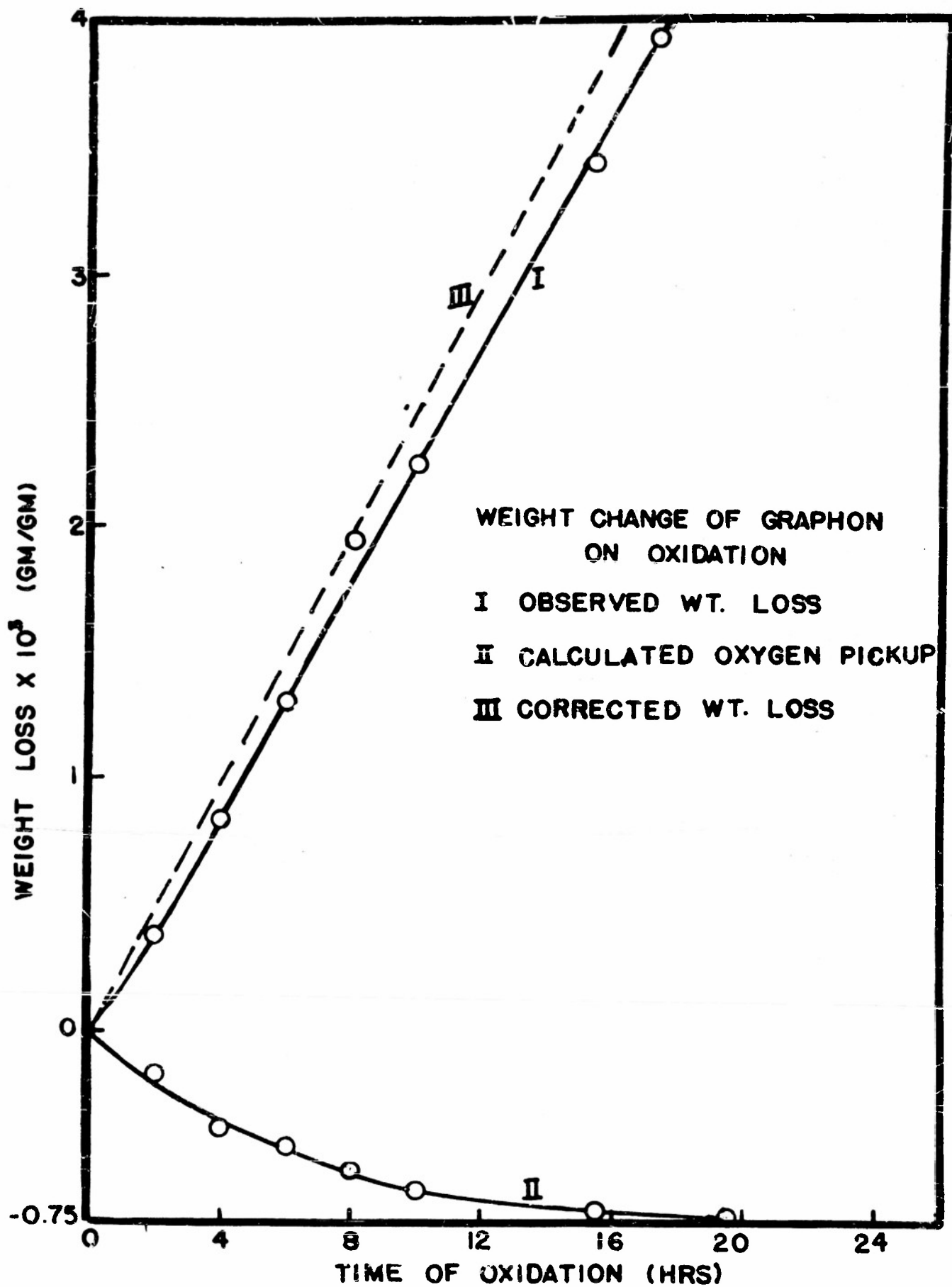
One of the objects of this investigation was to study the change in the nature of the water adsorption isotherm as the number of hydrophilic sites on the surface was increased. While in the preceding figure it would appear that the isotherm on the unoxidized surface was Type III and after 12 hours of oxidation

the isotherm was definitely Type II, this appearance is due simply to the difference in magnitude. The two isotherms are actually identical in shape up to the highest relative pressures measured (0.5-0.6). Indeed, if the isotherms are plotted in terms of $\theta(V/V_m)$ vs. p/p_0 , all of the oxidized samples as well as the unoxidized sample fall on a single curve. The shape of the isotherm is therefore not influenced by the fraction of the surface which is hydrophobic. If, as has been postulated (1,2) the adsorption of water by Graphon occurs by a clustering around hydrophilic sites, it would appear that on the original sample these heterogeneities were not isolated and randomly scattered about the surface but rather were grouped together in patches perhaps at the edges of the graphitic planes. Otherwise, it would be expected that increased adsorbate interactions would show up in the isotherm as the distance between hydrophilic sites decreased. Even with Sample A where 1/8 of the surface was made hydrophilic and the maximum distance between sites could be only approximately two molecular diameters, there was no essential difference in the shape of the isotherm from that of the unoxidized sample.

The weight change of Graphon on oxidation as observed with Sample D is shown graphically on the next page. The figure is very similar to the curves presented by Gulbransen and Andrew (8)

(8) E.A. Gulbransen and K.F. Andrew, Ind. Eng. Chem. 44, 1039 (1952).

for the oxidation of artificial graphite at 575°. Curve I repre-



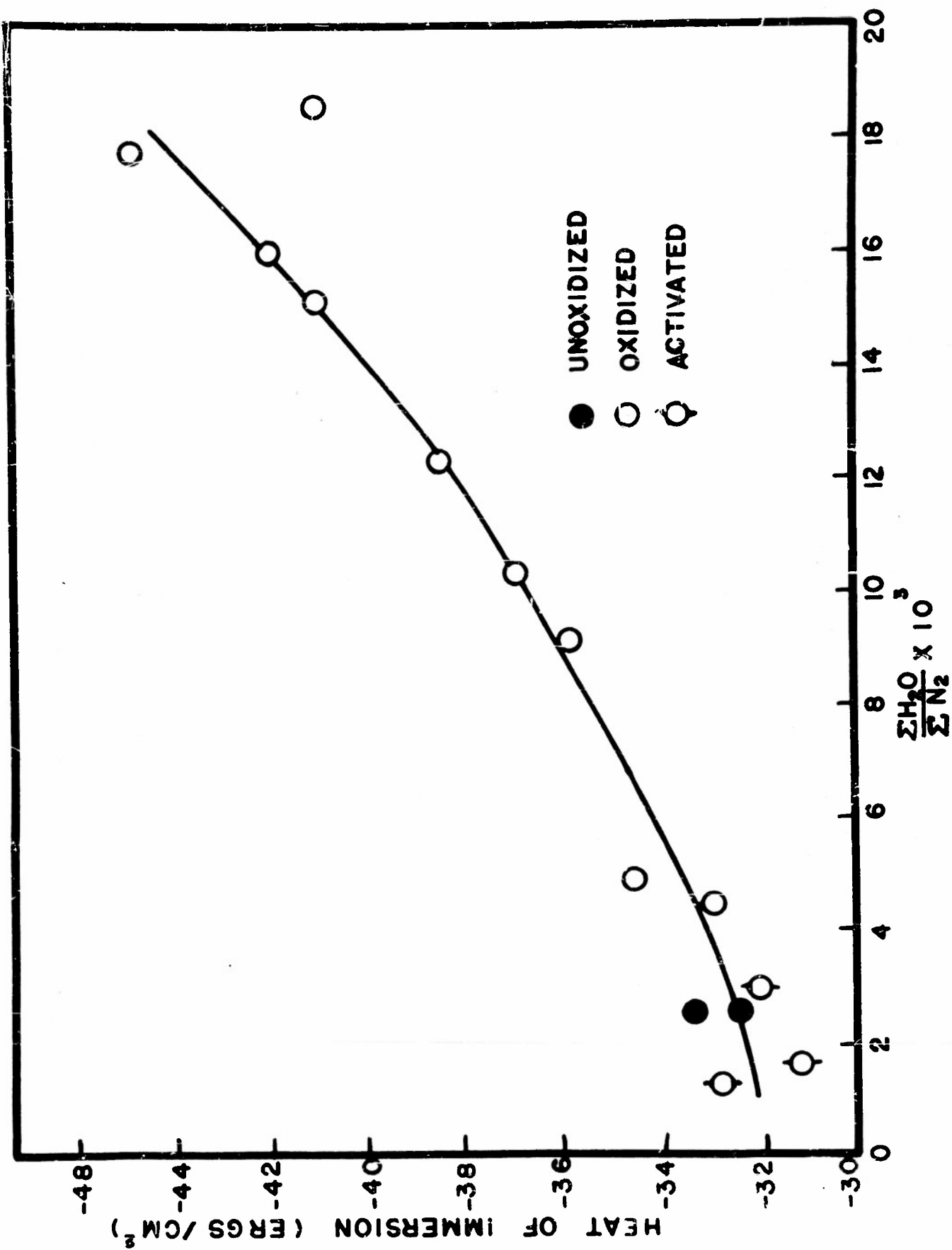
sents the observed loss in weight of the sample with increasing time of oxidation. Curve II is the calculated gain in sample weight due to the formation of surface oxide. This curve was calculated from the water adsorption V_m values on the basis of one water molecule to each CO surface site. Curve III therefore represents the actual weight loss after correction for the gain in weight due to chemisorbed oxygen. The curves indicate that the rate of formation of volatile oxides is essentially constant over a period of twenty hours, but that the rate of stable surface oxide formation decreases with time.

Heats of immersion in water were measured for a number of the samples after the various treatments. Additional samples not shown in Tables I and II were also used in this study. These data are plotted in the next figure in ergs per cm^2 of surface as measured by nitrogen adsorption against the fraction of the surface which was hydrophilic $\left(\frac{\sum H_2O}{\sum N_2} \right)$.

If the heat of wetting of the hydrophilic sites, h_o , and the hydrophobic carbon surface, h_c , remained constant with increasing amounts of surface oxide then a linear relation would be expected according to the equation:

$$h_I = \left(\frac{\sum H_2O}{\sum N_2} \right) h_o + \left(1 - \frac{\sum H_2O}{\sum N_2} \right) h_c$$

where h_I represents the observed heat of immersion. The best straight line drawn through the points would give $h_c = 31 \text{ ergs/cm}^2$



and $h_0 = 730$ ergs/cm.². The latter value is not unreasonable although somewhat higher than is usually obtained with hydrophilic surfaces. Since the θ experimental curve actually increases in slope it would appear that either h_0 increases or h_c decreases or that both occur as the percentage of hydrophilic sites increases. A decrease in h_c could be explained on the basis that the more energetic portions of the carbon surface would be most readily oxidized. However, water would interact with the carbon surface principally by non-polar van der Waals' forces and this interaction would be smallest on the carbon atoms (such as edge atoms) most readily oxidized. A more reasonable explanation is that h_0 increases due to increasing adsorbate interaction between neighboring patches of hydrophilic sites. This interaction would not show up in the isotherms except at relative pressures close to saturation.

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WORK NOW IN PROGRESS

A summary of current work undertaken in the period following that covered in the previous sections of this report is as follows:

1. As part of our study of the interaction of water with various types of surfaces, adsorption and heat of immersion measurements are being made with a bentonite clay. Thermodynamic calculations are to be made which should yield useful information concerning the surface properties of this material.

2. As a basis for the study of the inhibition of corrosion of metal surfaces, low temperature and room temperature oxidations of reduced nickel surfaces are being investigated by gas adsorption techniques.

3. A critical survey of the current data and theories of the role of various types of surface heterogeneities in corrosion has been prepared. The material will serve as a basis for a technical report to be submitted in the future.

4. Currently, a study of oxide-coated and reduced copper surfaces by physical and chemical adsorption techniques is being carried out. Further attention is to be directed to the nature of electronic defects in metals and in oxide films since this type of heterogeneity appears to influence strongly the oxidation process. Concurrently, the literature on organic corrosion inhibitors will be surveyed with the view toward studying treated metal samples by gas adsorption and calorimetric techniques.

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