

UNCLASSIFIED

AD NUMBER
AD092636
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; DEC 1955. Other requests shall be referred to Office of Naval Research, Arlington, VA 22203.
AUTHORITY
ONR ltr dtd 26 Oct 1977

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 92636

Armed Services Technical Information Agency

Reproduced by

DOCUMENT SERVICE CENTER

KNOTT BUILDING, DAYTON, 2, OHIO

This document is the property of the United States Government. It is furnished for the duration of the contract and shall be returned when no longer required, or upon recall by ASTIA to the following address: Armed Services Technical Information Agency, Document Service Center, Knott Building, Dayton 2, Ohio.

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

UNCLASSIFIED

AD NO. 92636
ASTIA FILE COPY

HETEROGENEITY OF SURFACES

Immersional Calorimetry and Adsorption Studies of

The Heterogeneous Nature of the Surfaces of Metallic and Nonmetallic Solids

Project Director - - - - A. C. ZETTLEMOYER

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

Office of Naval Research

Final Report

1 January 1949 to 31 December 1955

FC

Research Contract

N8onr-74300

Project Number

NRO-358-186

The Surface Chemistry Laboratory

Lehigh University

Bethlehem, Penna.

HETEROGENEITY OF SURFACES
Immersional Calorimetry and
Adsorption Studies
of
The Heterogeneous Nature of the Surfaces
of Metallic and Nonmetallic Solids

Project Director - - - - A. C. ZETTLEMOYER

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

Office of Naval Research

Final Report

1 January 1949 to 31 December 1955

Research Contract

N8onr-74300

Project Number

NRO-358-186

The Surface Chemistry Laboratory

Lehigh University

Bethlehem, Penna.

Table of Contents

	Page
Abstract	i
Introduction	ii
SECTION I. ADSORPTION STUDIES ON METAL V. OXIDATION OF NICKEL AT -78°, -22° and 26°	1
Introduction	1
Experimental	3
Results and Discussion	5
SECTION II. OXIDATION OF COBALT POWDER AT -78°, -22°, 0° and 26°. .	11
Introduction.	11
Experimental	13
Results and Discussion	15
SECTION III. STUDIES OF THE SURFACE CHEMISTRY OF SILICATE MINERALS	
III. HEATS OF IMMERSION OF BENTONITE IN WATER	23
Introduction	23
Experimental	25
Results and Discussion	27
Nitrogen, Ammonia, and Water Vapor Adsorption Isotherm	27
X-ray Diffraction Data	29
Heats of Immersion of Bentonite Sample in Water.	30

List of Tables

	Page
SECTION I	
Values Obtained from Use of Total Oxide Thickness	7
Values Obtained from Use of Increase in Oxide Thickness	8

SECTION II	
Values of V and W Obtained from Total Limiting Film Thickness . . .	18
Values of V and W Obtained from Limiting Film Thickness	19

List of Figures

Figure	Following Page No.
--------	--------------------

SECTION I	
1. Rate of Oxide Film Growth on Nickel at 26°	5
2. Limiting Oxide Film Thickness X_L as a Function of Total Film Thickness	6
3. Temperature Dependence of Total Limiting Film Thickness	7

SECTION II	
1. Rate of Oxygen Uptake by Cobalt Powder at 26°	15
2. Limiting Oxide Film Thickness X_L as a Function of Total Film Thickness	16
3. Limiting Oxide Film Thickness vs. Absolute Temperature	17

SECTION III	
1. Adsorption Isotherms on Bentonite	28
2. Swelling of Structural Units in Bentonite from X-ray Data	29
3. Heats of Immersion.	30
4. Heats of Desorption	34

ABSTRACT

I, II. The rates of oxidation of cobalt and nickel powders were measured in the thin film region at -78° , -22° , 0° and 26° . During the first oxidation of a reduced sample at each temperature, multiple oxide layers formed to some limiting thickness. This surface could be regenerated for further oxidation by heating in vacuo. Successive oxidations of the metallic sample were thus carried out, initially on the reduced sample, thereafter on the regenerated surface. The amount of oxygen adsorbed by the reduced and regenerated samples was an exponential function of time.

The theory of Mott and Cabrera for the growth of very thin oxide films did not satisfactorily explain the results. The governing kinetic factor for both nickel and cobalt was found to be the increase in oxide thickness rather than the total oxide film thickness. A mechanism based on the formation of metal lattice vacancies and their elimination by heating is proposed.

III. Nitrogen, ammonia and water vapor adsorption isotherms were measured on a Wyoming bentonite, a montmorillonite. In the BET range, nitrogen and water measured only the external area, whereas ammonia measured the internal area as well. The adsorption isotherms were monotonous and uninformative, but heats of immersion in water of samples equilibrated at increasing water vapor pressures reflected the regions at which the first and second layers of water formed between the platelets. X-ray data for the x-axis spacing confirmed these findings.

Comparison of the heat of immersion curves for samples activated at 25° versus 100° , and with the adsorption isotherms, revealed high energy sites for water adsorption. These are apparently exchange ion sites.

GENERAL INTRODUCTION

Atmospheric corrosion of many important metals depends on the ease of formation of oxide films on their surfaces and subsequent growth. In order to understand this phenomenon of corrosion more fully a study of the mechanisms of oxidation is necessary. In the past decade much effort has been directed toward studies of comparatively thick films and their mechanism of growth. However, the influence of the heterogeneous nature of the metal surface during the initial stages of reaction, i.e., in the film-thickness range of several Angstrom units, has received less than its deserved share of attention. Such studies have been and are being conducted at Lehigh University under Contract N8onr-74300.

Since this project has as its general aim the study of the nature of the various types of surface heterogeneity, special emphasis has been placed on this property and its role in corrosion and other surface phenomena. The investigation of surface heterogeneity in this laboratory has demonstrated that a metallic surface may have both a real physical heterogeneity, because of surface irregularities, and an apparent chemical heterogeneity, because of 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 in the surface. These three types of heterogeneity were shown (Technical Report No. 4) to be important to an understanding of the behavior of molybdenum towards oxygen at low temperatures (1,2).

-
- (1) F. H. Healey, J. J. Chessick and A. C. Zettlemoyer, J. Phys. Chem., 57, 178 (1953)
 - (2) J. J. Chessick, F. H. Healey and A. C. Zettlemoyer, J. Phys. Chem., 57, 912 (1953)
-

During the past year an investigation of oxygen sorption on nickel (3) has been carried out in this laboratory. Four temperatures, -195° , -78° ,

(3) Presented at the Colloid Division, American Chemical Society Cincinnati, Ohio, April 5, 1955

-22° , and 26°C. , were employed. Thereby, thin and progressively thicker oxide films could be studied. At -195° , during the first oxidation of a reduced nickel powder, apparently four portions of oxygen were adsorbed: (a) a monomolecular oxide layer adjacent to the metal, (b) a chemisorbed layer of O^{-1} ions, (c) "strong physical" and (d) ordinary physically adsorbed molecules. The strong physically bound molecules could be removed between -195° and -78° , and the chemisorbed ions could be converted to oxide at 350° ; thus the surface could be regenerated by high temperature treatment for further chemisorption of oxygen ions at -195° .

On exposure to oxygen at -78° , -22° , and 25° multiple oxide layers formed immediately. The outer chemisorbed layer was again believed to be chemisorbed ions which could also be converted to oxide by activation at 350° . The increase in depth of oxide on exposure to oxygen after each activation diminished as the oxide layer became thicker. Section I of this report summarizes the results obtained at these three temperatures. Contact potentials and work functions have been calculated from the theory of Mott and Cabrera at film thicknesses from 0-30 Å.

The oxidation behavior of cobalt (4) and its regeneration properties

(4) To be presented at the International Congress on Catalysis, Philadelphia, Pennsylvania, September 1956.

are discussed in Section II of this report. As for nickel, reasonable results for the contact potentials and work functions at different

thicknesses were obtained when the successive limiting thicknesses, rather than total oxide film thicknesses, were employed in the calculations.

Similar work on copper will be carried out in the near future, and oxidation in the thin film region at these temperatures will be studied.

While the greatest efforts of this project have always been directed toward a better understanding of the surface properties of metals, other phases of surface heterogeneity have received attention. For example, a thermistor calorimeter (5) operating near room temperature was designed

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

to measure heats of immersion. This apparatus not only increased the precision with which thermodynamic adsorption data could be obtained but also greatly widened the range of systems that could be studied. The study of the properties of oxide films (6) on different metals illustrates

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

the value of heat of immersion measurements in obtaining a quantitative measure of the porosity and hydrous nature of oxide coatings. The increased precision obtained by combining the two types of data, adsorption and calorimetric, is shown in the studies of a quite homogeneous surface, asbestos, (5), and a heterogeneous (to water) surface, Graphon (7,8).

(7) G. J. Young, J. J. Chessick, F. H. Healey and A. C. Zettlemoyer, J. Phys. Chem., 58, 313 (1954)

(8) F. H. Healey, Yung-Fang Yu and J. J. Chessick, J. Phys. Chem., 59 399 (1955)

A low temperature immersional calorimeter of novel design (9) has recently been constructed in this laboratory. It embodies a simple and

-
- (9) J. J. Chessick, G. J. Young and A. C. Zettlemoyer, Trans Faraday Soc., 50, 587 (1954)
-

accurate method for measurements of the heat of immersion of solids in liquid nitrogen at its boiling point from the volume of liquid vaporized when a clean sample is broken under the liquid. Low temperature heat of immersion measurements in liquid nitrogen have provided valuable data concerning the interaction between surface and adsorbate supplemental to the data obtained from gas adsorption studies with the use of inert nitrogen gas; and furthermore experimental verification of the important thermodynamic relationships developed by Harkins (10) and Jura and Hill (11)

-
- (10) W. D. Harkins, "Physical Chemistry of Surface Films", Reinhold Publishing Co., New York, N. Y. 1952, pp 199f.

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

were obtained.

To repeat, this project has as its general aim the study of the nature of the various types of surface heterogeneity; thus, a number of materials other than metals, with varying surface characteristics, have been included. A series of papers on silicate minerals was started with studies of asbestos (12, 13) and work on bentonite clay, using heats of

-
- (12) G. J. Young and F. H. Healey, J. Phys. Chem. 58 (10) 881-84 (1954)

- (13) F. H. Healey and G. J. Young J. Phys. Chem. 58 (10) 885-86 (1954)
-

immersion is given in Section III of this report and was published recently (14).

(14) Presented at the National Colloid Symposium, June 1955, Houston, Texas; A. C. Zettlemoyer, Yung-Fang Yu and J. J. Chessick, J. Phys. Chem. 59, 962-66 (1955)

In the case of bentonite, it was shown that heat of immersion values obtained as the mineral was exposed to greater and greater vapor pressures of water yielded important information concerning the surface heterogeneity and hydration of exchange ions on the surface as well as the important phenomenon of swelling. These pieces of information could not be obtained from gas adsorption data alone and they show the importance of supplementary heat of immersion data. Both adsorption and heat of immersion data are currently being collected for another clay mineral, attapulgite.

Another series of papers is being developed on the heterogeneity of hydrophobic surfaces. Several papers on Graphon, a graphitized carbon black, have been published (7,8), and work on Teflon has been completed on another contract (15).

(15) To be published in J. Phys. Chem. in April.

A critical survey of the current data and theories of the role of various types of surface heterogeneities in corrosion has been prepared. The paper, "Heterogeneity of Surfaces" was presented at the Gordon Research Conference on Corrosion held at Colby, New Hampshire, July 16-20, 1954, and the material in this paper will serve as the basis for a review article to be submitted for publication in the near future.

During the last months of the present contract, plans were made for the construction of a heat of chemisorption calorimeter. Construction will proceed under the new contract Nonr-1820(00). This added technique

should allow for a deeper understanding of systems already studied extensively by gas adsorption and heat of immersion.

Section I.

ADSORPTION STUDIES ON METALS V.
OXIDATION OF NICKEL AT -78° ,
 -22° and 26° INTRODUCTION

The initial stages of the oxidation of a metal are most conveniently followed at low temperatures. At room temperature and below, many metals in pure oxygen form a film of oxide less than $50 \text{ \AA}$ thick. During the first few minutes of exposure the film growth is rapid, but the rate soon falls to a very low value. Results of a number of workers on the low temperature oxidation of copper, iron, aluminum and silver have been summarized by Kubashevski and Hopkins (1).

-
- (1) O. Kubashevski and B. E. Hopkins, "Oxidation of Metals and Alloys," Butterworth Scientific Publications, London, 1953, p. 131.
-

A theory covering the mechanism of growth in thin oxide films has been formulated by Cabrera and Mott (2)

-
- (2) N. Cabrera and N. F. Mott, Rep. Progr. Phys. 12, 163 (1948-9).
-

and applied by Rhodin (3) to his data on the oxidation

-
- (3) T. N. Rhodin, Jr., J. Am. Chem. Soc. 72, 5102 (1950)
-

of single crystals of copper.

Nickel, like copper, forms a p-type semiconductor and would be expected to follow the same mechanism of growth in the thin film region. This mechanism presupposes the existence of a very thin oxide film on which oxygen is adsorbed and converted to ions by tunneling of electrons. The high potential field set up between the metal-oxide interface and oxide surface is sufficient to induce unidirectional cation movement. Rhodin

found the theory of Mott and Cabrera to be valid with some limitations to oxide films of 5-50 Å in thickness.

Dell and Stone (4) studied the adsorption

(4) R. M. Dell and F. S. Stone, Trans. Faraday Soc. 50, 501 (1954).

of oxygen on nickel oxide films of 25-180 Å at 20° C. No rate data was given but they did report that a 25 Å film adsorbed a monolayer of oxygen in five minutes, and further that by heating in vacuo this adsorptive power of the oxide surface could be regenerated. The regeneration was not due to desorption, but, according to the authors, to incorporation of the adsorbed oxygen as nickel oxide. Regeneration of oxide films on nickel and copper has been reported earlier by Russel and Bacon. J. Am. Chem. Soc. 54, 54 (1932). Lanyon and Trapnell (5) have recently reported a

(5) M. A. H. Lanyon and B. M. W. Trapnell, Proc. Royal Soc., A227, 387 (1955)

study of the kinetics of slow oxygen uptake on evaporated metal films. They interpreted their data on Cu and Fe in terms of the theory of Mott and Cabrera, but for Rh, Mo, W, Ta, and Zn, they proposed a mechanism based on the interchange of adsorbed oxygen atoms with underlying metal atoms.

The purpose of the present study was to investigate the nature of the growth and regeneration of very thin films (0-30 Å) of oxide on nickel. Because of the regeneration phenomenon, it was possible to study the kinetics as a function of initial oxide thickness.

EXPERIMENTAL

A previous article (6) described the nickel sample

-
- (6) A. C. Zettlemoyer, Yung-Fang Yu and J. J. Chessick, J. Phys. Chem. **59**, 588 (1955).
-

adsorption apparatus, reduction train, and the purification of hydrogen, argon and helium. Oxygen was dried by passing it through a charcoal trap immersed in a dry-ice, acetone mixture and a column of MgSO_4 .

Reduction of surface oxide was accomplished by passing dry hydrogen at atmospheric pressure through the sample at 350° for three hours. Reductions continued beyond this point caused a loss of sample weight of less than 0.005% per hour. The sample was degassed at 400° for two hours to remove hydrogen.

For each series of oxidation rate studies a fresh sample, reduced under identical conditions, was used. The rates of oxidation were measured at -78° , -22° , and 26° . Physical adsorption of oxygen was negligible at these temperatures. At least two parallel series of oxidations were run at each temperature, with each series consisting of from five to nine alternating oxidations and activations. The activations were made by heating the sample for two hours at 350° in the closed evacuated system. The temperature was controlled to within 5° and the time within five minutes. Activations at 400° gave greater regeneration, but were not used because of the possibility of sintering.

The first activation of each sample produced a small pressure build-up. The evolved gas did not re-adsorb when the sample was cooled to room temperature. Since the amount of gas was negligible in comparison to the amount of oxygen taken up in the subsequent oxidation, the gas was probably residual hydrogen driven off during the first oxidation. No detectable

pressures were produced by later activations. Werner Scheuble (7), has found

(7) Werner Scheuble, Z. Physik, 135, 125-40 (1953)

that H on the surface of nickel did not affect the adsorption of oxygen.

The range of oxide film thickness was generally 0-30A° and in a few cases a thickness of 50A° was reached. The rate of adsorption was slightly dependent on pressure; in all runs reported here the pressure was maintained in the range 5-7 mm. Hg by controlled small doses of oxygen.

Surface areas were determined by argon adsorption at -195°. The first oxidation produced a 5% increase in area. Subsequent activations and oxidations of the sample caused no further area change.

RESULTS AND DISCUSSION

The kinetic data obtained at -78° , -22° and 26° on freshly reduced nickel and on regenerated oxide surfaces were of the same general type. The initial rate of oxidation was rapid but after about ten minutes the rate had decreased to a low value. Plots of volume of oxygen adsorbed against log time were linear after the first five minutes and continued so for at least twenty-four hours, the longest times measured.

In Fig. 1 the results at 26° are plotted in terms of an average oxide film thickness calculated from the surface area, the bulk NiO unit cell length of $4.2 \text{ \AA}$, and assuming, like Dell and Stone (4), the presence of equal areas of (100), (110) and (111) faces of NiO.

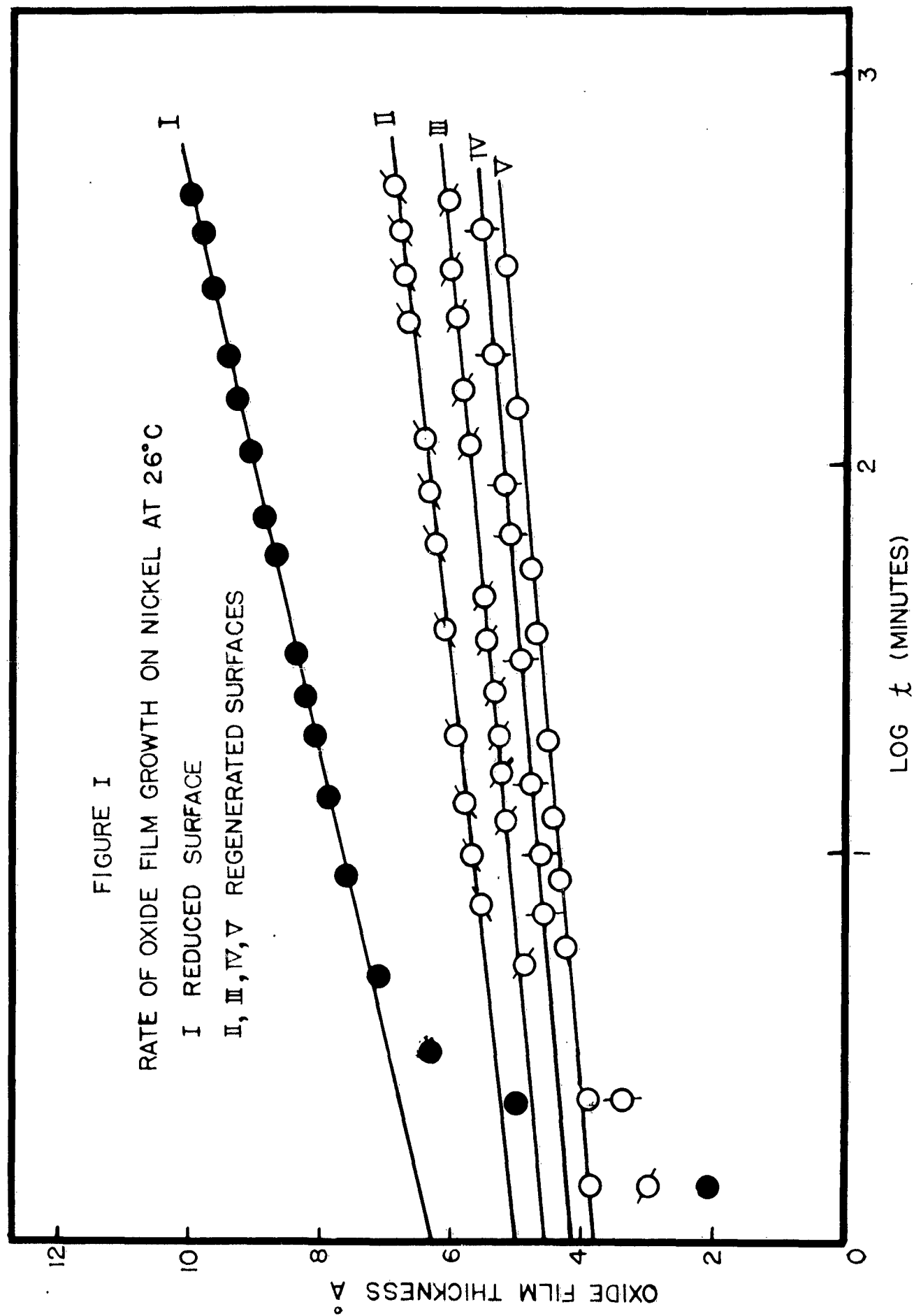
The thickness in Angstroms was obtained from the relation

$$x = \frac{\text{vol. ads.} \times 1.99}{\text{area} \times 0.204}$$

where 1.99 is the average length in $\text{\AA}$ of one layer of NiO (assuming equal distribution of principal planes) and 0.204 represents the ml. of O_2 required to form a monolayer of NiO per m^2 of surface. The approximate number of layers of oxide can thus be obtained by dividing the values of x by 1.99.

Curve I is the data obtained on freshly reduced nickel. Prior to each of oxidations II-V the sample was activated at 350° for two hours in vacuo. The ordinate gives the thickness of oxide formed only during that particular oxidation. The total thickness of oxide is obtained by summing the results of I-V. At the end of oxidation V the total thickness was about 35° .

A limiting film thickness X_L was defined, in accordance with the convention used by Cabrera and Mott and by Rhodin, as the thickness at which the growth rate had decreased to $10^{-13} \text{ cm./sec.}$, or about one atom



layer per day. The values of ΔX_L calculated from the slopes and intercepts of the curves in Fig. 1 and the corresponding data at -22° and -78° are shown in Fig. 2. The ordinate represents the limiting increase in film thickness during the particular oxidation for an oxide film of initial thickness given by the abscissa. The values for $X=0$ thus represent the limiting thickness of the oxide layer on reduced nickel and varied from 11 Å at 26° to 8 Å at -78° . As the oxide film thickened, the predicted limit of additional growth decreased, but the value of ΔX_L appears to approach an almost constant value except at -78° . The data was carried to about 35 Å so as to overlap the lower limit of the film thicknesses studied by Dell and Stone (4).

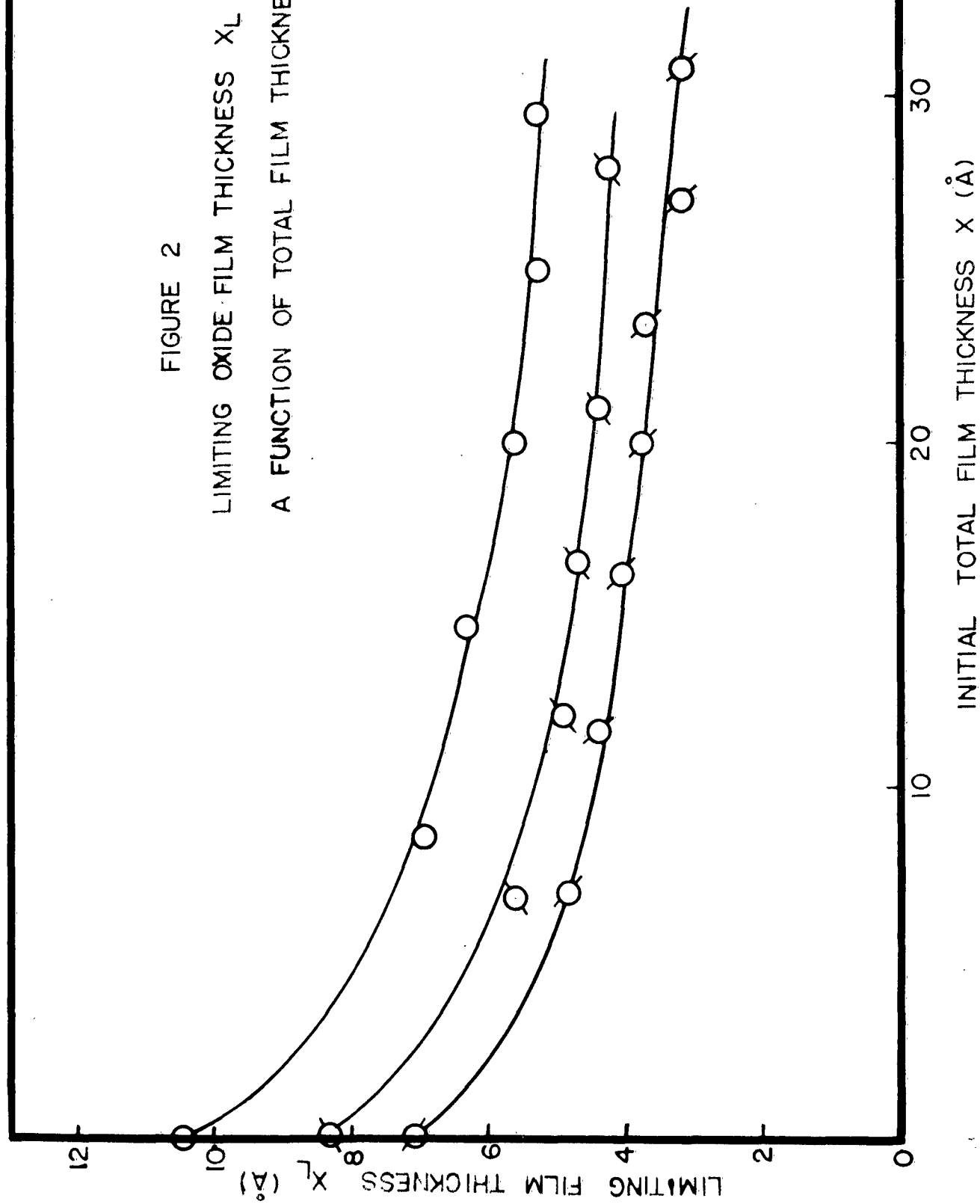
According to the theory of Cabrera and Mott (2) the important variable in determining the kinetics of growth of very thin oxide films is the potential field across the film. The field $F=V/X$ where V is the contact potential between the metal and the oxygen ions adsorbed on the oxide surface. This field is supposed to be the driving force for cation escape from the metal lattice. As the film thickens the field decreases, if V is constant or decreases, and the limiting thickness X_L , as defined above, is given by the equation:

$$X_L = Vaq/(W-39kT) \quad (1)$$

where a is the distance a cation must travel from a position in the metal lattice to a cation vacancy in the oxide lattice; q is the charge per cation; W the activation energy for cation escape from the metal to the oxide; k is the Boltzmann constant; and T the absolute temperature. The factor 39 comes from the arbitrary definition of X_L .

From Eq. (1) the value of W and of the product aV can be obtained from a plot of $1/X_L$ vs. T . It is clear from the above theory that this value of X_L should refer to the total film thickness. While the theory does not consider the phenomenon of regeneration of oxide, it is of

FIGURE 2
 LIMITING OXIDE FILM THICKNESS x_L AS
 A FUNCTION OF TOTAL FILM THICKNESS



considerable interest to apply the equation to the data on nickel for various film thicknesses.

In Fig. 3 the values of $1/X_L$ are plotted against T for various initial film thicknesses. X_L is obtained by adding the initial thickness to the predicted limiting growth during a particular oxidation. The experimental points show a slight consistent deviation from the straight lines which were used to obtain the values in Table I. The contact potentials V , were calculated by assuming the distance a , in Eq. (1), to equal $3.98\text{\AA}$.

TABLE I

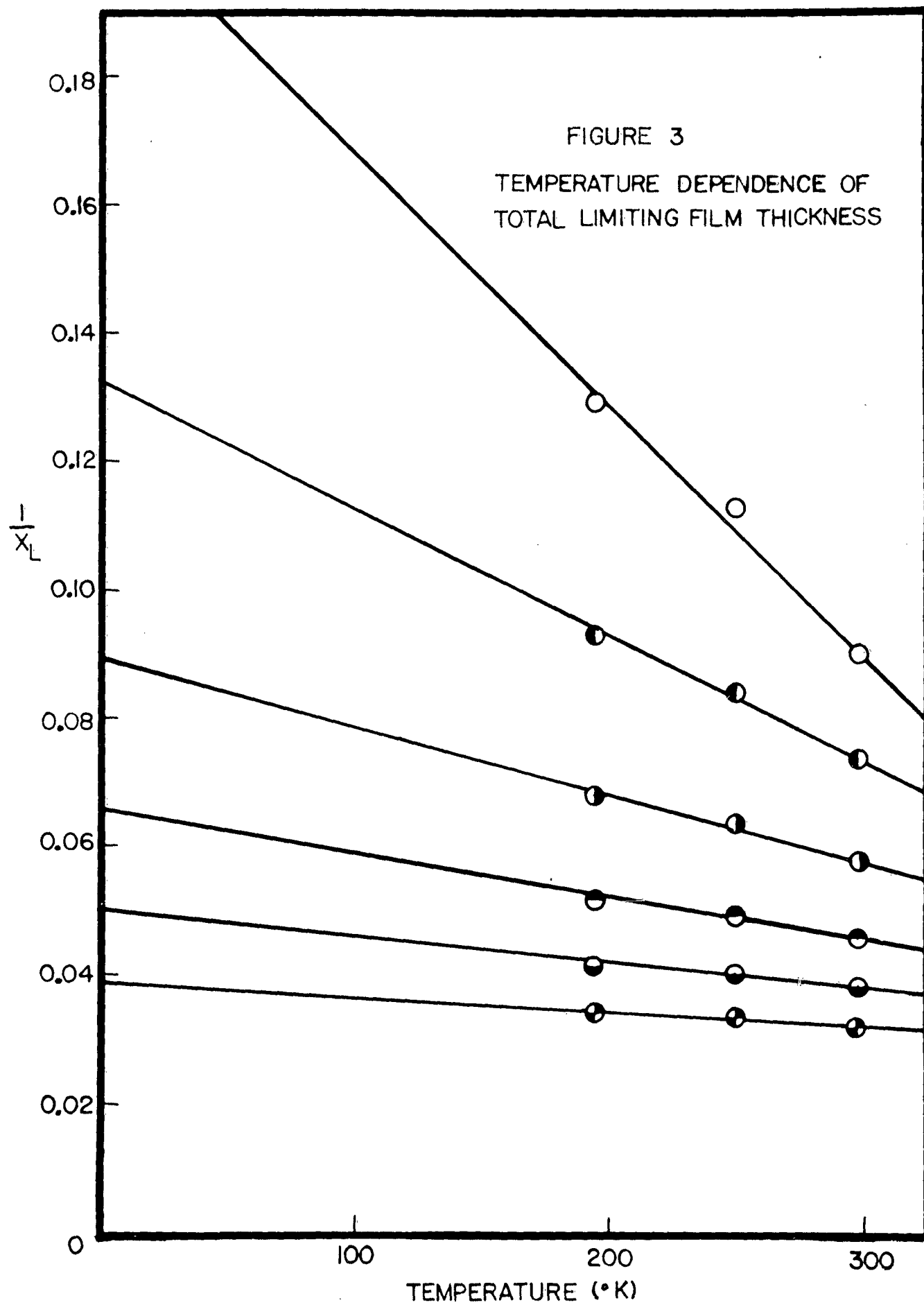
Values Obtained from Use of Total Oxide Thickness

<u>Initial Film Thickness</u>	<u>Work Function</u>	<u>Contact Potential</u>
<u>$X (\text{\AA})$</u>	<u>$W (\text{e.v.})$</u>	<u>$V (\text{volts})$</u>
0	1.67	0.92
5	2.23	2.01
10	2.81	3.75
15	3.26	5.90
20	4.31	10.26
25	6.05	18.55

The initial values of W and V are quite reasonable, but as the film thickens W does not remain constant, as would be expected from the theory, and V approaches absurd values. Clearly there is something wrong in this application of the theory to the data on regenerated oxide films. The fault may be due either to the concepts of the theory or to some effect on the oxide film produced by the regeneration process.

As can be seen in Fig. 1 the kinetics of the oxidation are not much affected by the total film thickness. After each regeneration the rate is but slightly less than the previous run. The governing variable appears to be the growth in thickness during the particular run, that is, ΔX , rather than X . Similarly there is a trend toward constancy of ΔX_L whereas X_L as a limiting total thickness seems to have no real significance.

Eq. (1) was therefore applied to the data with ΔX_L used in place



of X_L . From the plots of $1/\Delta X_L$ vs. T the values of W and V in Table II were calculated as before.

TABLE II

Values Obtained From Use of Increase in Oxide Thickness

<u>Initial Film Thickness</u>		
<u>X (Å)</u>	<u>W (e.v.)</u>	<u>V (volts)</u>
0	1.67	0.92
5	1.66	0.68
10	1.61	0.55
15	1.64	0.51
20	1.64	0.47
25	1.63	0.44
30	1.59	0.40

The values in Table II appear quite reasonable. W remains essentially constant and independent of film thickness. V decreases rapidly for the first 10 Å of growth but thereafter decreases only slowly. The results on Ni may be compared with the data of Rhodin for the first oxidation of copper which gave $W=1.13$ e.v. and $V=0.83$ V. Rhodin's value is higher than the reported contact potential of 0.7 for copper-cuprous oxide.

Any one of the results in Table II might provide reasonable support for the theory of Cabrera and Mott. The difficulty arises from their hypothesis that the rate of oxide growth is governed by the potential field which should depend on the total oxide thickness, and provides no mechanism for the regeneration process. It might be argued that the regeneration involves almost complete destruction of the oxide surface previously formed. That this possibility is extremely unlikely is evidenced by (1) no evolution of oxygen, (2) no change in surface area during the activation at 350° . Further, if the process involved a recrystallization of compressed oxide to bulk oxide lattice occurs, it can do so only once. Partial regeneration of films of even 180Å° thickness was noted by Dell and Stone (4).

The mechanism proposed by Dell and Stone to explain chemisorption of oxygen on nickel oxide films and their regeneration by heating involves

- (1) formation of surface O^- and Ni^{+3} ions in oxide
- (2) on heating, Ni atoms pass from metal into oxide and incorporate O^- as bulk $Ni^{+2} O^\bullet$.

Their mechanism cannot explain the formation of more than a monolayer since they state cationic mobility is absent in nickel oxide at 20° . In the range of film thickness studied by us, however, more than one layer of oxide is formed even at -78° . Thus, our results follow neither the theory of Cabrera and Mott nor the mechanism of Dell and Stone.

To explain our results in the range 5-30 Å of oxide the following mechanism is proposed. Oxygen is adsorbed on the oxide and converted to ions by tunneling of electrons. The electrostatic field between the metal-metal oxide interface and the oxygen ions at the oxide surface promote cation diffusion. This process continues until the vacancies in the metal lattice reach a point where further escape of cations is negligible. Regeneration by heating involves a physical rearrangement of the metal-metal oxide interface to eliminate the vacancies in the metal lattice.

This mechanism explains qualitatively the reason that the oxidation rate is primarily influenced by the increase in film thickness rather than the total thickness. The field is considered at all times to be sufficiently strong to promote rapid cation diffusion although as the oxide layer increases the diffusion is less rapid.

It does not appear that a satisfactory test of the Cabrera-Mott theory can be made on the basis of a single oxidation. The regeneration phenomena provides a very useful additional variable, the total film thickness, to be introduced. Results in this laboratory have

been obtained for copper and cobalt and will be published in the near future.

Section II.

OXIDATION OF COBALT POWDER AT -78° ,
 -22° , 0° and 26° INTRODUCTION

The reaction between a metal and oxygen is one of the most common phenomena encountered. Yet the mechanism of the formation and growth of the oxide film is still not understood, particularly in the region of very thin oxide films. There remains, too, a lack of sufficient, reliable data for the initial stages of oxidation.

In a recent theoretical development, Mott and Cabrera (1) have

(1) Cabrera, N. and Mott, N. F., Reports Prog. Phys. 12, 163 (1949).

attempted a mathematical explanation of the oxidation in the very thin film range from a few Angstroms to about $100 \text{ \AA}$. They have successfully applied their concepts to the experimental results of aluminum oxidation. Rhodin (2) also established the validity of their concepts for the oxida-

(2) Rhodin, T. N., Jr., J. Am. Chem. Soc., 72, 5102 (1950).

tion of single crystals of copper. Recently, Trapnell and Lanyon (3)

(3) Lanyon, M. A. H. and Trapnell, B. M. W., Proc. Roy. Soc., 227A, 387 (1955).

have found in their study of the oxidation of evaporated films that iron and copper follow the Mott and Cabrera mechanism at low temperatures; the metals, tungsten, molybdenum, rhodium and tantalum, however, do not.

Russell and Bacon (4) first reported that reduced nickel and

(4) Russell, W. W. and Bacon, O. C., J. Am. Chem. Soc., 54, 54 (1932).

copper surfaces, apparently completely oxidized at a given temperature, can be regenerated for further oxidation by heating in vacuo. These workers were not able to evaluate the surface area of their samples; consequently the phenomenon could not be completely understood. Dell and Stone (5) also found this regeneration in their study of oxygen chemisorp-

(5) Dell, R. M. and Stone, F. S., Trans. Faraday Soc., 50, 501 (1954).

tion on an oxide-coated nickel surface, and proposed a mechanism based on the semi-conductor property of the oxide to explain the regeneration process. Unfortunately, their work did not include a study of the initial stages of oxidation of the bare metal.

The present investigations were designed to study the oxidation and regeneration of nickel, cobalt and copper samples in the range of oxide thicknesses up to $30 \text{ \AA}$ by gas adsorption techniques. The oxidation of nickel at 26°C and below was reported in Section 1 of this report. Here the results of study of the oxidation of cobalt using similar techniques is reported. Oxidation of copper, and oxygen adsorption on all three metals at -195° will be reported later.

EXPERIMENTAL

The cobalt powder was prepared in this Laboratory by thermal decomposition of C. P. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 400° under reduced pressure. The cobalt oxide was then screened through at 350 mesh sieve and reduced with dry hydrogen at 350° for seventeen hours to constant weight. A thirty gram sample was prepared and stored for use in subsequent oxidation studies. Suitable portions of this sample were again reduced on the adsorption apparatus at 350° for four hours prior to each series of adsorption measurements. The completion of this reduction was indicated by a weight loss of less than 0.005% per hour. The sample was then degassed at 400° for two hours to remove hydrogen.

The Orr type adsorption apparatus consisted of an oil manometer containing Apiezon "B" oil. The reduction train, and the purification of hydrogen, argon and helium have been described previously (6). Oxygen was

(6) Chessick, J. J., Yu, Y. F., Zettlemoyer, A. C., J. Phys. Chem., 59, 588 (1955).

dried by passing through a charcoal trap immersed in a dry ice-acetone mixture and a MgSO_4 drier.

The initial rate of oxygen uptake was instantaneous and pressures fell rapidly to zero. The rate then slowed down and finite pressures could be measured. The rate of oxidation was measured by following the decrease in pressure with time. It was found that the rate was slightly dependent on the pressure, consequently the pressure was maintained in a range of 5-7 mm Hg. by controlled dosage. The amount of oxygen chemisorbed was calculated from PVT data.

Fresh samples were used for each series of oxidations. At least two parallel series of runs were made at each temperature to avoid gross

errors. Five to nine successive oxidations and activations were carried out on a given sample in a series of runs at one temperature. The first oxidation occurred on the reduced sample, the second and following oxidations occurred on the same sample regenerated by activation. The activation process was conducted by heating the sample in a closed evacuated system. The activation temperature was $375^{\circ} \pm 5^{\circ}$ maintained for two hours. For a few activations, the oxidized sample was heated to 400° or 450° to determine the temperature dependency of the regeneration process. There was no gas evolved during activation.

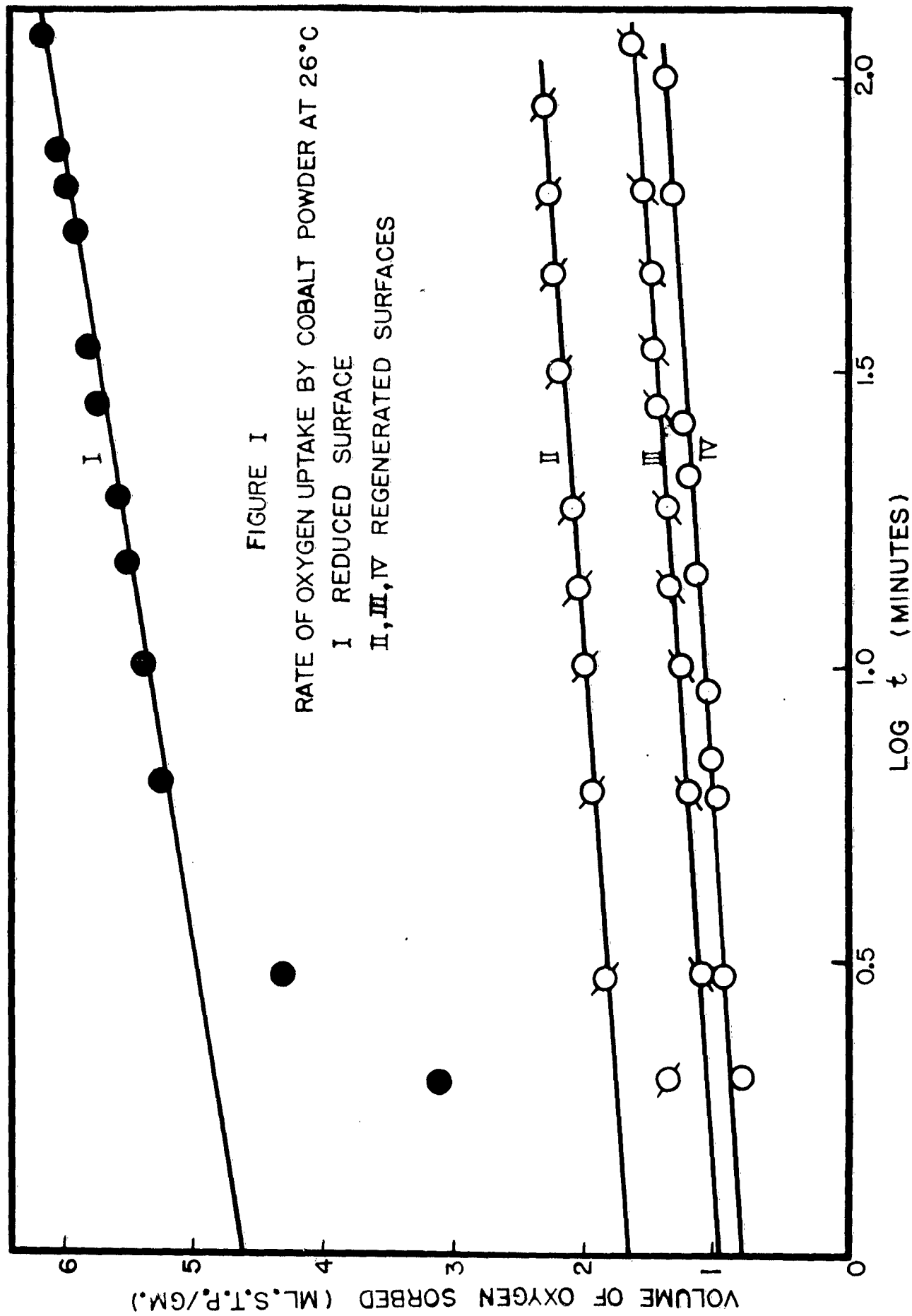
Surface areas of the reduced and oxide-coated surfaces were determined by argon adsorption at -195° and calculated by the conventional BET method.

RESULTS AND DISCUSSION

The rate curves for oxidations of reduced and regenerated cobalt samples at -78° , -22° , 0° and 26° were all the same type. The oxygen uptake, shown in Figure 1 for oxidation at 26° , decreased exponentially with time after the first few minutes. A plot of the amount adsorbed vs. $\log t$ was found to be linear up to periods of 24 hours. Oxidations for longer periods were not carried out. An oxide-covered surface could be regenerated for further oxidation by heating at elevated temperatures in vacuo. Oxidation on the regenerated surfaces followed the same pattern found for the initial oxidation of a reduced surface. The degree of regeneration increased with increasing activation temperature.

The amounts of oxygen sorbed was converted by calculation into oxide film thickness by assuming: (1) The surface oxide film has the same crystalline structure as the bulk oxide most stable at the oxidation temperature; (2) That equal areas of the (100), (110) and (111) faces were present on the surface.

A limiting thickness X_L , defined by Mott and Cabrera (1) and used by Rhodin (2), was calculated for each oxidation. This thickness was so chosen that the rate of growth of oxide was 10^{-13} cm./sec., or about one layer per day. It was obtained by extrapolating the rate plots in Figure 1 to the point corresponding to the limiting thickness. In Figure 2, the limiting thickness for oxidation carried out at four different temperatures are plotted against the initial total film thickness, x , prior to that run. The total initial film thickness is the sum of the film thicknesses formed in the previous oxidations. Total film thicknesses up to $35 \text{ \AA}$ were studied at all four temperatures. For example, the value of X_L at $x = 0$ represented the limiting thickness on a reduced sample. The values of X_L decreased



sharply, initially, then levelled off as the oxide film thickened at a given temperature.

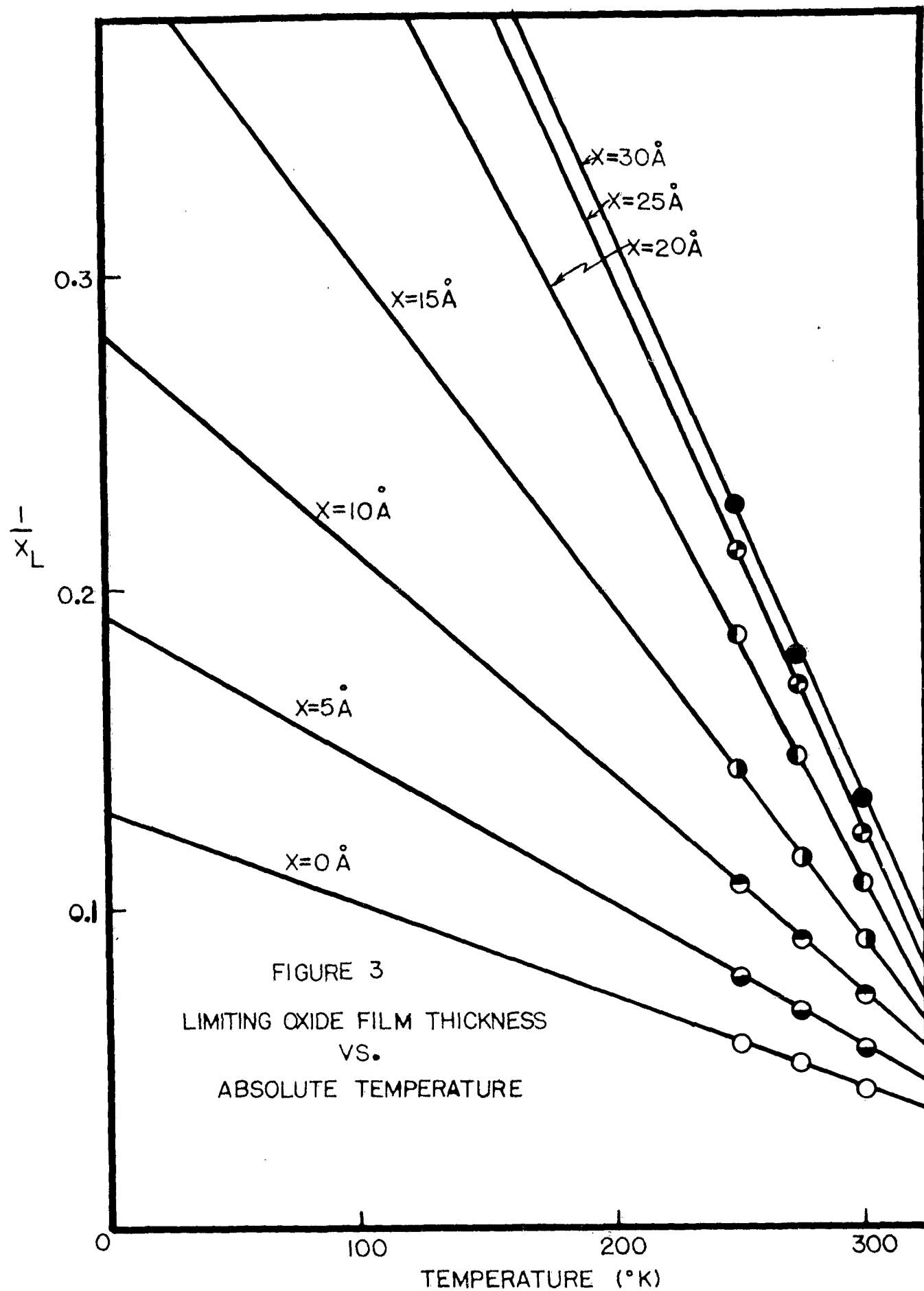
The amount of oxygen chemisorbed decreased with decreasing temperature except at -78° . This anomaly was not found when similar measurements were made with nickel and copper. A tentative explanation may be that at this low temperature, oxygen may be somewhat strongly physically adsorbed in addition to that required for oxide formation. This physical adsorption could account for the larger amounts of oxygen taken up at this temperature on cobalt oxide. However, more experimental work is definitely needed before any decision can be made.

The results for oxidations at -22° , 0° and 26° were treated according to the recent theory of Mott and Cabrera (1). This theory assumes that oxidation at low temperatures, where the cations do not have enough thermal energy to diffuse, can proceed as follows: The oxygen first adsorbs on the surface with dissociation; electrons then leave the metal and diffuse outward to the oxygen either by the tunnel effect or by a thermionic mechanism. An electrical potential is thus set up across the oxide film and if the film thickness is less than $100 \text{ \AA}$, the resultant field is strong enough to cause forced migration of the cations through the film to combine with oxygen. By an elaborate derivation, Mott and Cabrera obtained the following equation for the rate of oxidation:

$$\frac{dx}{dt} = A \exp \left(\frac{x_1}{x} - \frac{W}{kT} \right) \quad (1)$$

where x is the film thickness at time t ; k the Boltzman constant; T the absolute temperature; W is the sum of heat of solution of cation in the oxide and the activation energy for cations to diffuse through the oxide. The term, x_1 , a critical oxide film thickness, is defined by the equation:

$$x_1 = naV/kT, \quad (2)$$



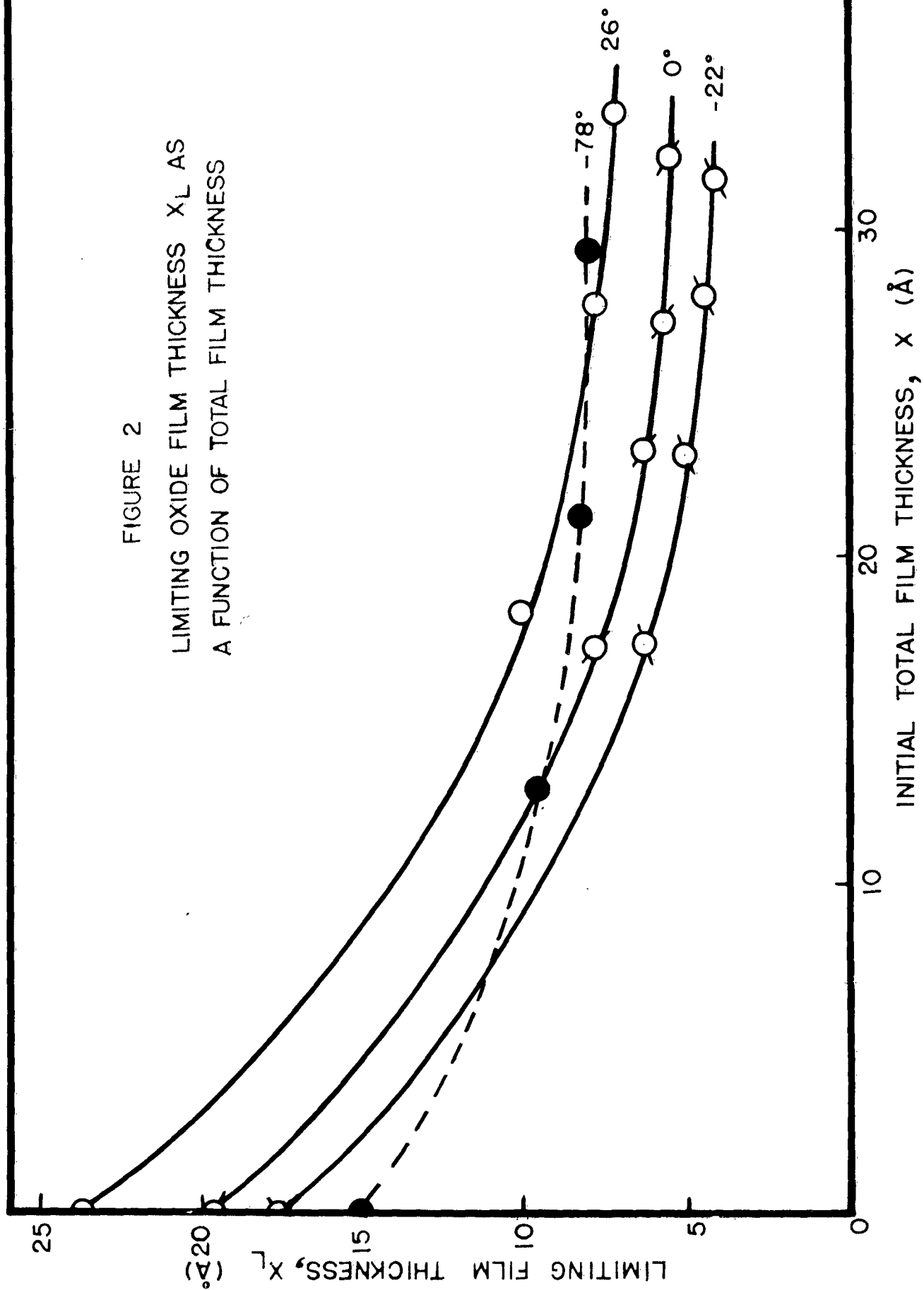
where n is charge per ion, a the average distance between sites, and V the electric contact potential difference existing through the oxide film. In the very thin film region, equation (1) may be integrated, and was shown to be a logarithmic function. The term A is a constant which is dependent on the concentration of sites on the surface, the densities of the oxide and the metal, and also the frequency factor for the oxidation of this reaction. By introducing the term X_L , defined above, the equation can be transformed:

$$\frac{1}{X_L} = \frac{W}{naV} - \frac{39kT}{naV} \quad (3)$$

where 39 is a constant dependent on the rate at X_L and on the conversion factor A . An average value of $3.78 \text{ \AA}$ for a was calculated for cobalt, this value is based on the average interplanar distances assuming equal areas of the three major faces present on the surface.

If it is assumed that regeneration does not disturb the oxide already present on the surface, then further oxidation should be governed by the transference of cobalt cations from the metal-oxide interface to the oxide-gas interface where reaction takes place. The rate would be dependent on the total film thickness if the theory of Mott and Cabrera were valid. The limiting thickness then would be the sum of the defined limiting thickness X_L for a particular oxidation plus the thickness of the oxide layers previously formed. These total limiting thicknesses for successive oxidations, designated as X_L' , were calculated for oxidations at -22° , 0° and 26° . A plot of $1/X_L'$ against absolute temperature T yielded good straight lines as expected from equation (3). The values of W and V were then evaluated from the slopes and intercepts, and are listed in Table I. The V and W values for nickel oxidation are included in the table for comparison. The values of both W and V unexpectedly increased with increasing film thickness. By a similar estimation as that made by Mott (1), the value of V should be in

FIGURE 2
 LIMITING OXIDE FILM THICKNESS x_L AS
 A FUNCTION OF TOTAL FILM THICKNESS



the order of one volt; that of W about 1 to 2 e.v. A comparison of these values with the results above, indicated that the theory of Mott may be valid for the initial oxidation on a reduced surface but not for successive oxidations of the regenerated surfaces where abnormally high values of V and W were obtained. Possible reasons for the discrepancies in V and W values will be discussed below.

Table I

Values of V and W Obtained from Total Limiting Film Thickness, X_L

Initial thickness, x (Å)	Contact potential, V (volts) COBALT	Work function, W (e.v.)
0	0.96	1.45
10	1.35	1.61
15	1.83	1.78
20	2.80	2.18
25	3.64	2.30
30	5.28	2.70
NICKEL		
0	0.92	1.67
5	2.01	2.23
10	3.75	2.81
15	5.90	3.26
20	10.26	4.31
25	18.55	6.05

The values of V and W were recalculated in a similar manner using values for the limiting thickness X_L formed during each individual

run. The results are listed in Table II. This time values of both V and W appeared reasonable. W was fairly constant except for a slightly higher value found for the oxidation on the reduced surface. The values after the

Table II

Values of V and W Obtained from Limiting Film Thickness X_L

Initial thickness, x (Å)	Contact potential, V (volts) COBALT	Work function, W (e.v.)
0	0.96	1.45
5	0.62	1.37
10	0.41	1.32
15	0.23	1.26
20	0.18	1.20
25	0.16	1.20
30	0.15	1.21
NICKEL		
0	0.92	1.67
5	0.68	1.66
10	0.55	1.61
15	0.51	1.64
20	0.47	1.64
25	0.44	1.63
30	0.40	1.59

first oxidation might be expected to be constant since they represent the sum of heat of solution of cation in the oxide and the activation energy of cation diffusion, both independent of the film thickness. Similar results

were obtained in the study of nickel oxidation as shown in the second part of Table II. It appears that the theory of Mott and Cabrera can be successfully applied to the results of the oxidations of nickel and cobalt in the thin film range if the limiting thickness, X_L , formed during a given oxidation is used in the calculations rather than the total limiting film thickness, X_L' . Nevertheless, it is difficult to understand why the total oxide film thickness is not the governing kinetic factor when the basic concepts underlying the theory of Mott and Cabrera are considered.

The following mechanism can be used to explain qualitatively the results found for the oxidation of cobalt. During the oxidation of a reduced surface, direct combination of oxygen and cobalt is thermodynamically feasible. This is supported by the fact that oxygen can chemisorb at -195° if contacted with the bare metal. After the surface is covered with a monomolecular film of oxide, the oxidation may be supposed to follow a mechanism somewhat similar to that proposed by Mott (1). It can be visualized as a three step process: (1) Oxygen atoms adsorb on the surface. (2) Electrons leave the metal migrating outward to the oxygen to form oxygen anions through the tunnel or thermionic effect. (3) An electric potential is built up across the film between the cations and the adsorbed oxygen anions. This potential would be of the order of one volt. In the case of thin films, and particularly in the region of only a few layers of oxide, the electric field will be so strong that the cations, even though they do not have enough thermal energy to leave the lattice, will be pulled out to react with the oxygen anions. This process will continue with a decreasing rate due to the decrease in field strength as oxide thickness increases. Another factor which also reduces the field strength and can slow down the reaction is the formation of lattice vacancies left behind by the diffused cations. As more oxide is formed, larger number of vacancies are created at the metal oxide

interface which would form a cavity barrier against cation diffusion. The creation of vacancies in effect increases the effective oxide film thickness, or more precisely reduces the field strength.

During activation several processes are possible: (1) Desorption of oxygen or decomposition of oxide. (2) Recrystallization or a change of metal concentration at interface. (3) Cracking of the oxide layer due to misfit of the initial oxide over the metal surface atoms. Since there was no gas evolution or weight loss observed during the activation, the possibility of oxygen desorption is excluded. Argon adsorption was followed during various stages of the oxidation-activation processes; there was no appreciable area change observed. Thus cracking of the surface is unlikely.

Based on these facts the following mechanism of regeneration is suggested. During activation, the required thermal energy is supplied to the ions and metal atoms. Cations move out from the metal-oxide interface and react with oxygen anions left on the surface. Since activation is conducted in a highly evacuated system, and a further supply of oxygen is not available, the electrical potential across the film is destroyed. By means of the increased thermal mobility, the lattice vacancies at the metal-oxide interface are filled either by oxide moving inward or metal atoms moving outward. Thus, preparation is made for the development of a strong field again when oxygen is chemisorbed on the regenerated surface.

After the oxide film has grown sufficiently thick at a given temperature, the field across the oxide is insufficient to cause cation migration without activation. Chemisorption of oxygen, however, does not stop. Now oxygen chemisorbs with dissociation, and is converted into O^{2-} anions by tunneling of electrons. The maximum oxygen adsorption now would be equivalent to that necessary to form one oxide layer. Activation allows

cation migration at the elevated temperature with formation of a cobalt oxide layer upon union with the chemisorbed oxygen anions.

Dell and Stone (5) have already discussed this mechanism in their study of the chemisorption of oxygen on oxide-coated nickel powders. These workers found that only a monolayer of oxide formed during activation which followed oxygen chemisorption at 20° in the film thickness range from about 25 to 110 Å. This behavior might be expected also with cobalt, although here the film thickness at which this mechanism alone operates is certainly greater than 25 Å.

Section III.

STUDIES OF THE SURFACE CHEMISTRY OF SILICATE MINERALS. III.
HEATS OF IMMERSION OF BENTONITE IN WATERINTRODUCTION

The first studies in this series dealt with the surface chemistry of chrysotile asbestos fibers (1,2) as revealed by gas adsorption and heat

-
- (1) G. J. Young and F. H. Healey, J. Phys. Chem. 58, 881 (1954).
 (2) F. H. Healey and G. J. Young, J. Phys. Chem. 58, 885 (1954).
-

of wetting measurements. In the present paper, results of similar studies of Wyoming bentonite, a montmorillonite, are described. Future papers will deal with kaolinite, attapulgite and other silicate minerals.

Many previous workers have compared the adsorption of nitrogen and water vapor by silicate minerals. Recently, for example, Keenan, Mooney and Wood (3,4,5) studied a series of kaolinites and a montmorillonite

-
- (3) A. G. Keenan, R. W. Mooney and L. A. Wood, J. Phys. Colloid Chem., 55, 1462, (1951).
 (4) R. W. Mooney, A. G. Keenan and L. A. Wood, J. Am. Chem. Soc. 74, 1367 (1952).
 (5) R. W. Mooney, A. G. Keenan and L. A. Wood, J. Am. Chem. Soc., 74, 1371 (1952).
-

by this approach. Heats of immersion of these minerals have been measured also as indicated in the summary given by Grim (6). Unfortunately, both

-
- (6) R. E. Grim, "Clay Mineralogy", McGraw-Hill Book Company, Inc., 1953, p. 184.
-

these techniques have not previously been used on the same samples. When the heats of immersion were measured, adsorption isotherms and surface areas were not measured, and vice versa.

In addition, no previous work has been reported for bentonite in which the heats of immersion were followed as the mineral was exposed to greater and greater water vapor pressures. As for asbestos, the limitations of isotherm measurements in deducing the surface properties of bentonite become apparent when the results of the heats of immersion measurements are considered. Comparison and interpretation of adsorption results on clays such as bentonite are also complicated by: (1) the number of exchange ion sites, (2) the type and number of adsorbed ions, (3) the different amounts of internal area exposed on swelling by different polar molecules, and (4) the presence of variable amounts of impurities.

EXPERIMENTAL

X-ray diffraction studies of the bentonite sample employed in this investigation (7) showed it to be mainly montmorillonite containing

(7) Supplied by the American Colloid Company, Merchandise Mart Plaza, Chicago 54, Illinois. The clay is predominantly a sodium clay and is sold commercially under the trade name Volclay.

small amounts of feldspar, quartz, and kaolinite. The sample was extracted repeatedly with distilled water, dried at 80° and crushed in an agate mortar before adsorption and heat of wetting measurements were made.

Water vapor adsorption isotherms were determined gravimetrically at 25° for a sample degassed at 25° for 48 hours and for another sample degassed at 100° for 24 hours. Equilibrium pressures were read on an oil manometer filled with Apiezon "B" Oil. Equilibrium was attained within 24 hours for relative pressures up to about 0.50; beyond this relative pressure much longer times were required.

A conventional volumetric adsorption apparatus was employed for the ammonia and nitrogen adsorption studies. The gases were Mathieson Pure Grade and were fractionated into storage bulbs before use. The sample bath temperature for the ammonia adsorption was held at ca. -32°. This temperature was maintained constant by use of an equilibrium mixture of solid and liquid bromobenzene; the presence of the solid phase was assured by a cold finger tube containing dry ice. The bath for nitrogen adsorption was liquid nitrogen.

The calorimeter used in the heat of immersion studies has been described (8). Values for the heats of immersion were obtained for

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

degassed bentonite samples and for samples equilibrated at continuously increasing amounts of adsorbed water. As for the isotherms, samples evacuated under two different conditions were studied: one series was evacuated at 25° for 48 hours, the other evacuated at 100° for 24 hours. The samples for heat of immersion studies that were exposed to water vapor were prepared on an adsorption apparatus and sealed off after the desired equilibrium pressure was attained. Care was taken to insure that the temperature of the sample was not altered during the sealing-off process. The heat values were calculated on the basis of the dry sample weight and were corrected for the heat of breaking of the sample tubes.

X-ray data on the exposed samples were taken with an automatic recording G. E. XRD-3 X-ray unit. The specimen holders were filled with the bentonite samples and then equilibrated in desiccators containing saturated salt solutions giving the desired relative pressure of water vapor. The specimen holders were then covered with a very thin formvar film so that there would be no change in the water content of the samples during the X-ray measurements.

RESULTS AND DISCUSSION

Nitrogen, Ammonia, and Water Vapor Adsorption Isotherms. --

Bentonite is an expanding lattice type clay. The principal structural components are alternate layers of hydrated metal oxide and silicon-oxygen tetrahedron sheets. These layers are normally loosely held together by coordinately bound water molecules. When polar molecules are taken up between these layers, the familiar swelling phenomenon takes place. Thus, in the present investigation both water vapor and ammonia adsorbed on the external surface and also entered between the ultimate platelets which comprise the primary particles of the bentonite. Nitrogen, on the other hand, was only adsorbed on the external surface (9).

-
- (9) S. Brunauer, "The Adsorption of Gases and Vapors", Princeton University Press, Princeton, N. J., 1945, p. 357.
-

The external surface of the bentonite calculated by the BET equation from nitrogen adsorption data was $34.5 \text{ m}^2/\text{g}$. Grinding the sample after washing and drying increased the area from an original value of $11.7 \text{ m}^2/\text{g}$. Mooney et. al. (4) have also reported that sample preparation affected the surface area due to breaking up of some of the organized bentonite particles. The nitrogen isotherm was a typical Type II and similar to that for a non-porous solid.

The ammonia adsorption data showed that there was a much larger uptake of this gas in the BET range of relative pressure (p/p_0 0.05 to 0.35) than could be explained on the basis of the external area alone. Past this range of relative pressure the isotherm showed a very gradual increase in the amount adsorbed until a relative pressure of about 0.85 where the adsorption again increased strongly. Because of the large differ-

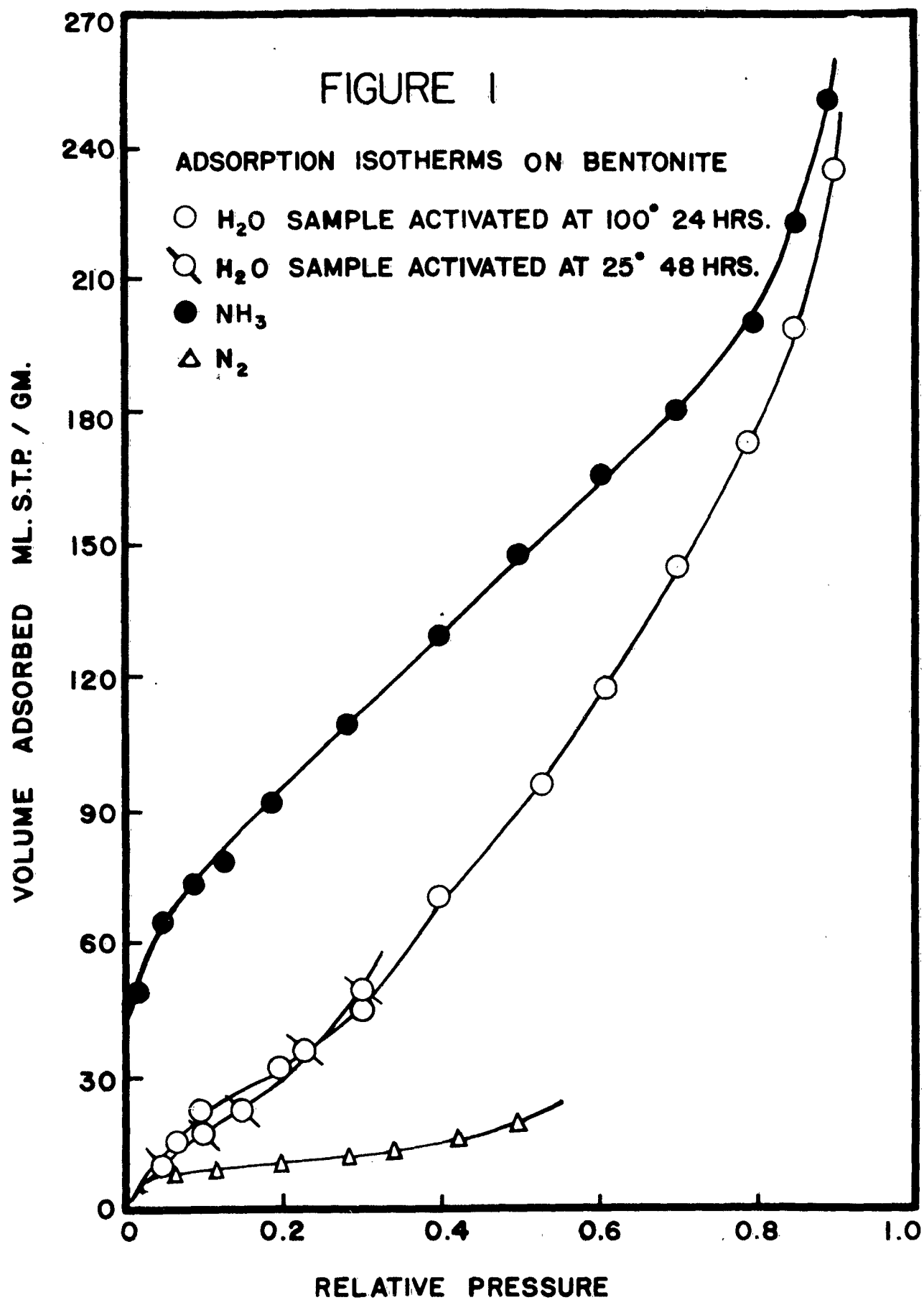
ence in the amount of ammonia adsorbed compared to water or nitrogen, it is evident that in the BET range of relative pressure ammonia not only adsorbs on the external bentonite surface but is also imbibed between the platelets, a number of which comprise each bentonite particle. The area calculated from the ammonia V_m amounted to $295 \text{ m}^2/\text{g}$. This value represents the external area and half the internal area since only one molecular layer of ammonia will be expected to adsorb between platelets in this region of relative pressure. Thus the total surface area is obtained by subtracting the nitrogen area which gives the external area from twice the ammonia monolayer area. A total area of $556 \text{ m}^2/\text{g}$. was estimated in this manner.

Isotherms for the adsorption of water vapor on bentonite samples evacuated at 25° and 100° are shown plotted in Figure 1. Unlike ammonia, water vapor was adsorbed principally on the external surface of the clay in the BET range of relative pressure. These results are contrary to those of Mooney (4) and Hendricks (10) who found that water vapor adsorbed on

(10) S. B. Hendricks, R. A. Nelson and L. T. Alexander, J. Am. Chem. Soc. 62, 1457 (1940).

both the external and internal surfaces of their samples in this relative pressure range. The water vapor adsorption isotherms are not particularly revealing; they give no information concerning the total area nor do they indicate the swelling phenomenon which occurs when the water molecules begin to enter between the platelets.

Isosteric heats of desorption, calculated from water vapor desorption isotherms at two temperatures, reveal little further about the swelling (4) than do the isotherms. Heats of immersion at various amounts of water adsorbed, however, reveal internal adsorption quite clearly as will be indicated later.



X-ray Diffraction Data. -- The swelling of bentonite by imbibing water between the platelet structure is illustrated by the X-ray data of Figure 2. The c-axis spacing (the axis perpendicular to the platelets) is shown as a function of the relative pressure at which the samples were equilibrated. As is generally found, the water uptake between platelets was not a continuous function of relative pressure but occurred at rather distinct relative pressures. Also, the water entered between the platelets in integral numbers of monomolecular layers. Thus, for the bentonite employed in this investigation, the first layer of water molecules entered at about 0.3 relative pressure and a second layer at about 0.7 relative pressure.

The X-ray data supported the isotherm data that water vapor adsorption in the BET region of relative pressure was primarily on the external surface. That is to say, there was no change in the c-axis spacing until a relative pressure of 0.3 was reached.

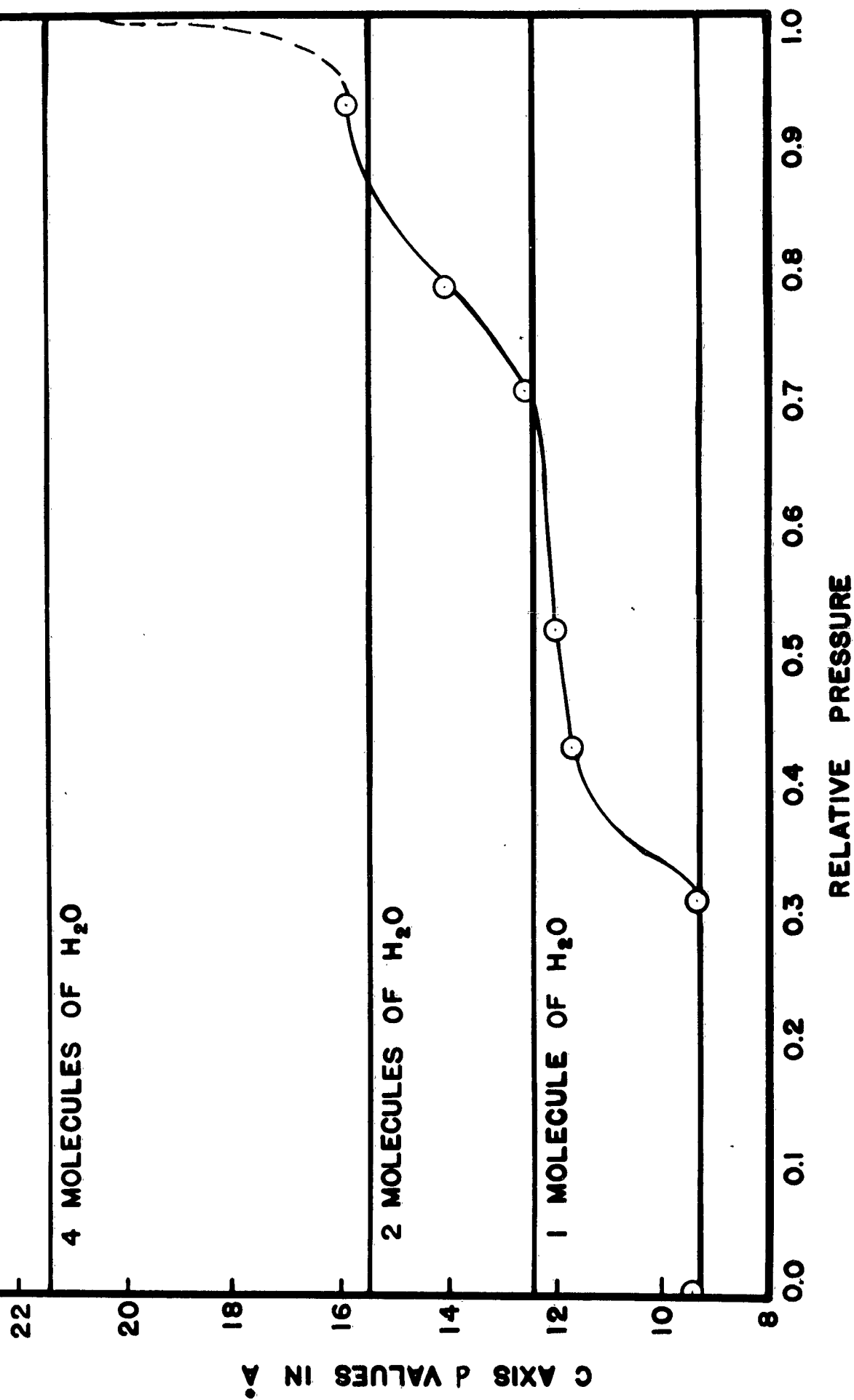
The water vapor adsorption isotherms did not strongly reflect the stepwise water uptake shown by the X-ray studies. No doubt simultaneous and continuously increasing adsorption on the outer surfaces and at the edges of the platelets masked the water uptake between the layers. In addition, while the majority of platelets swelled at a rather definite pressure in each step, the imbibing of water between the platelets was probably distributed over a fairly broad relative pressure region. These processes combined to give rather smooth water vapor adsorption isotherms with only indistinct changes of slope indicating internal sorption.

It has been reported (11) that certain montmorillonite samples

(11) W. F. Bradley, R. E. Grim, and G. L. Clark, Z. Krist. 97, 216 (1937).

FIGURE 2

SWELLING OF STRUCTURAL UNITS IN BENTONITE FROM X-RAY DATA



imbibe 4 layers of water molecules between platelets at very high relative pressures. No definite evidence of this was found in the present work up to relative pressure of 0.99. However, there did appear to be a slight increase in the c-axis spacing at very high relative pressures over the 15.5 Å that represents two water layers between platelets. The finding that the imbibed water is limited to two molecular layers is in agreement with the work of Hendricks et al. (10).

Heats of Immersion of Bentonite Samples in Water. -- The heats of immersion of bentonite samples evacuated at 25° and 100° are plotted in Figure 3. The heats are shown as a function of the relative pressure at which the samples were equilibrated with water vapor before the immersion measurements were made. The values of the heats of immersion are plotted on a per gram basis rather than per unit surface area because of the complication of the increase in internal area with swelling.

As indicated previously, in the case of activation at 25°, the initial adsorption of water vapor occurred primarily on the external bentonite surface. This adsorption process is reflected by the heat of immersion data for the initial portion of the lower curve for 25° activation in Figure 3. In fact, this curve in the region from zero to 0.25 relative pressure is similar in appearance to typical heat of immersion curves for heteropolar, non-porous solids like TiO_2 (12). The initial rapid

(12) W. D. Harkins, "Physical Chemistry of Surface Films", Reinhold Publishing Co., New York, New York, 1952, P. 231.

fall of the curve denotes the disappearance of the bare solid surface and the formation of a solid-adsorbed film interface as the amount pre-adsorbed was increased. Completion of an external monolayer of adsorbed water vapor is shown by the first plateau where further amounts of adsorbed water

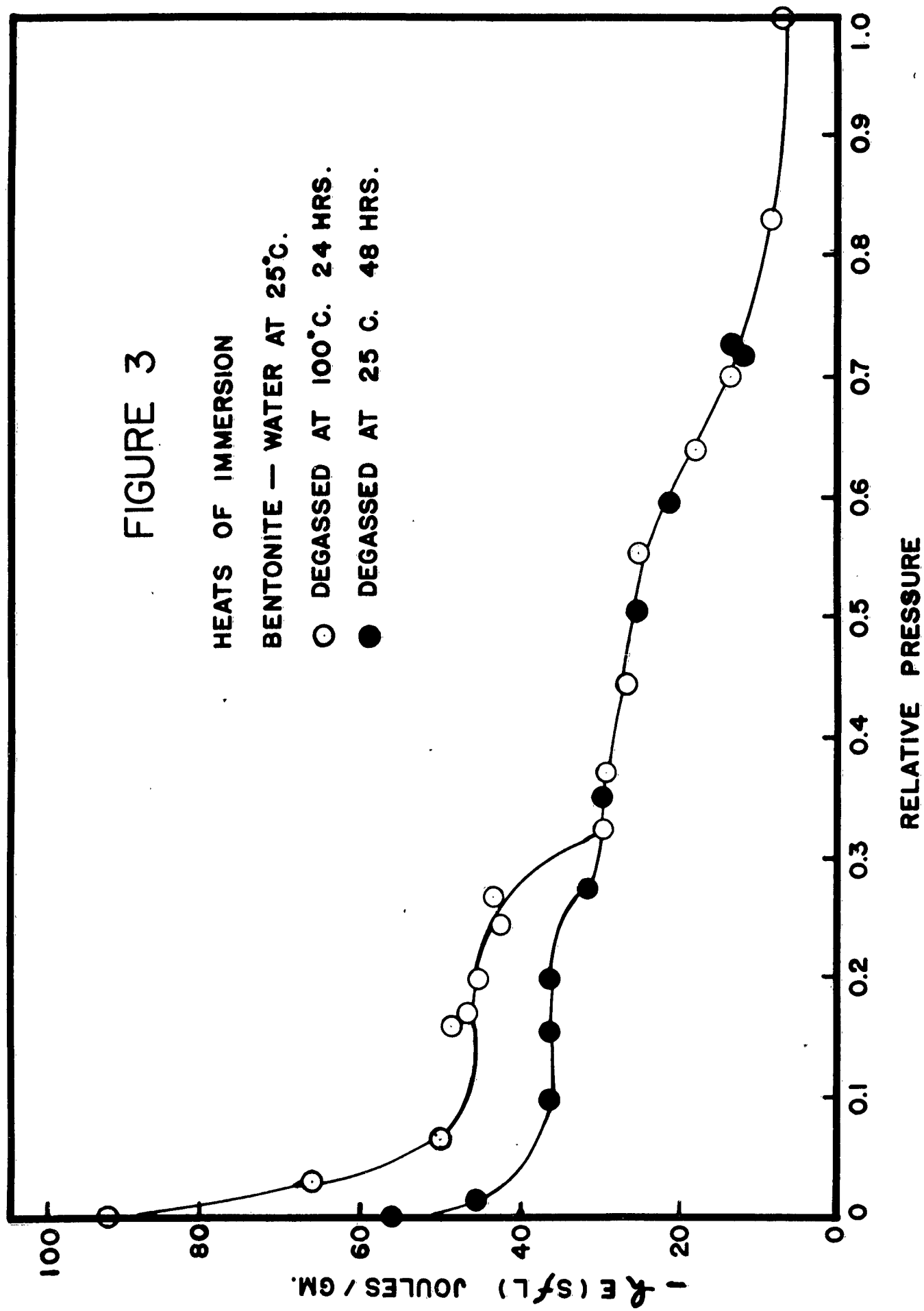
FIGURE 3

HEATS OF IMMERSION

BENTONITE — WATER AT 25°C.

○ DEGASSED AT 100°C. 24 HRS.

● DEGASSED AT 25 C. 48 HRS.



affected the immersion values only slightly.

When the heat of immersion values for the sample evacuated at 25° are expressed on the basis of unit area of external surface, the difference in the heat of immersion between the clean bentonite surface and the surface covered with a monolayer of water amounts to about -575 ergs/cm². This magnitude is about 250-300 ergs/cm² higher than the corresponding values for other heteropolar surfaces. Therefore, either the clay surface is more energetic, adsorption wise, or another phenomenon in addition to physical adsorption such as hydration of exchange ion sites on the external surface of the clay was taking place. If hydration did occur on adsorption it is somewhat surprising that the original water of hydration on the exchange ion sites was removed by evacuation at 25°. An absolute magnitude of the heat of immersion of the bentonite clay external surface is, of course, impossible to obtain experimentally because of the endothermic swelling process which also occurs on immersion.

The first inflection in the heat of immersion curve for activation at 25° occurred at approximately the same relative pressure as the first dimensional change shown by the X-ray data in Figure 2. This inflection is therefore interpreted to reflect the heats of swelling and of sorption on the internal bentonite surface due to the entrance of the first monolayer of water between structural platelets. The immersion curves for the two different activations merged during this introduction of the first water layer between platelets.

The heat of immersion curve for activation at 100° (upper curve) paralleled the lower curve up to a relative pressure of about 0.25. Differences are the heat of immersion of the clean bentonite surface which was now much higher and the sharper decrease in the initial stages up to a relative pressure of ca 0.05. However, the water vapor adsorption isotherms for the two different activations did not indicate large

differences in the amount of water vapor adsorbed. Therefore, the initial rapid change in slope for activation at 100° represents adsorption on more energetic sites than were present after evacuation at 25°. The more energetic of these adsorption sites are presumably exchange ions on the external surface which can be hydrated; dehydration resulted from activation at 100°.

It is of considerable significance that the heat of immersion curves for the two different activations do not coincide until a relative pressure of about 0.3 is reached. Apparently, a part of the water removed by activation at 100° could not be replaced by adsorption until this relative pressure was reached. However, it will be recalled that at 0.3 relative pressure the first monolayer of water was imbibed between the platelet structure. These findings suggest that activation at 100° not only produces highly energetic sites on the external surface but also between the platelets. These energetic adsorption sites on the internal surface are also presumably dehydrated exchange ions.

It is of interest now to consider the magnitude of the difference in energies of adsorption for the two activation conditions. The difference in the initial heat of immersion values (at zero relative pressure) represents the wetting of additional sites uncovered by the 100° activation. Presumably these sites are exchange ion positions and were activated by removal of hydrated water. The additional amount of water desorbed from the bentonite by the 100° activation amounted to 0.0122 g.H₂O/g. clay. If this additional water removed at 100° is reversibly readsorbed, then the heat effect for readsorbing would amount to 12.6 Kcals/mole H₂O.

After the heat of immersion curves for the two different activation curves merged at a relative pressure of ca. 0.3, they became identical up to saturation. The second plateau in the heat of immersion curve in

Figure 3 again represented primarily multilayer adsorption on the external surface. This relative pressure region of the plateau corresponded roughly to the relative pressure region in Figure 2 where the X-ray data show little change in the c-axis dimensions, i.e. no increased swelling of the bentonite particles. The heat of immersion curve changed only slightly in this region since the energy of adsorption for multilayer formation is nearly constant and the magnitude of the heat of immersion would be expected to change only as the fraction of water adsorbed in this region compared to the total adsorption changes.

At a relative pressure of about 0.6 the heat of immersion curves again changed slope sharply. Here multilayer formation on the external surface was still proceeding, but now the second molecular layer of water molecules started to form between the platelets. Again this process was gradual for energy barriers preventing entrance of a second imbibed water layer were evidently not the same for all particles. It is probable that when one platelet pair was spread sufficiently for the entrance of the second water layer this second molecular layer formed immediately. Therefore, any endothermic heat process for the spreading of platelets was probably over-shadowed by the exothermic heat of adsorption of water molecules between the platelet pairs. This interpretation of the relative pressure region from ca. 0.6 to 0.8 was also supported by X-ray data which show that the c-axis changed dimension sufficiently to admit one more molecular layer of water molecules between the platelets in this region.

The final leveling of the heat of immersion curve represented primarily multilayer adsorption on the external surface. The X-ray data showed no change in c-axis dimensions in this relative pressure region, and no change in the internally imbibed water was to be expected. The surface area in this region calculated by the Harkins (13) absolute method was

(13) W. D. Harkins, *op cit*, p. 273.

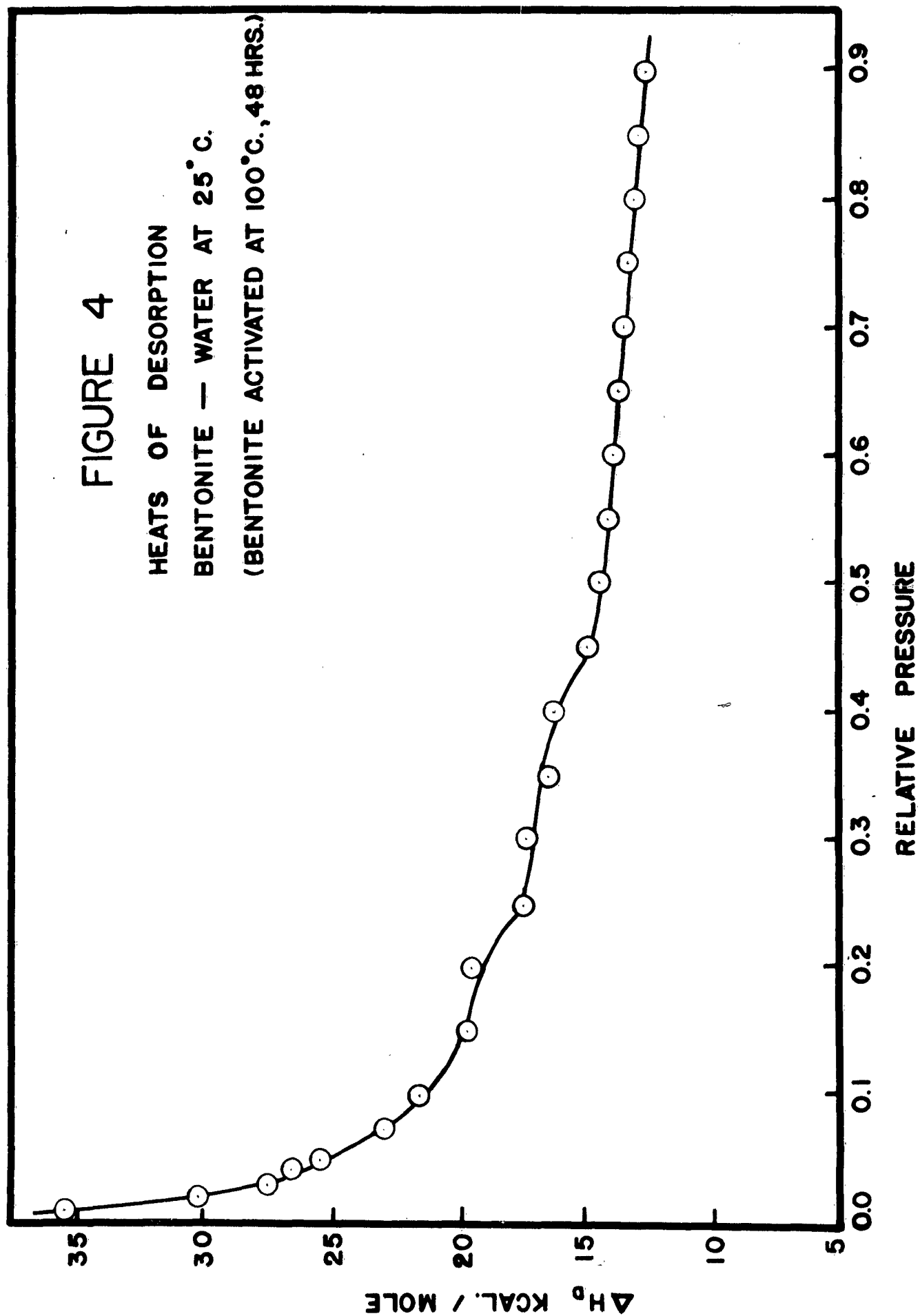
44 m²/g. This value is about 30% larger than the nitrogen area of the dry bentonite. The reason for this difference is that the bentonite particles were now swollen and hence had a larger external area than when dry. This increase in area was also calculated on the basis of the change in the c-axis dimensions given by the data in Figure 2; a value of 43 m²/g. was obtained, in excellent agreement with the value calculated from heat data by the Harkins absolute method.

The heat of desorption curve of water vapor from bentonite is given in Figure 4. This curve was obtained from the heat of immersion data by dividing ($h_{SL} - h_{SfL}$) by the number of moles of water adsorbed per gram at the coverage used to obtain the h_{SfL} value and adding to this the energy of vaporization of the adsorbed water at 25°. It is significant that this curve does not reflect the changes occurring on the uptake or removal of water in such detail as the heat of immersion curves. The heat of desorption curve was based on the heat per mole of adsorbed water and since the isotherm data are reflected in this calculation the curve is smoothed out in much the same manner as the isotherms in Figure 1.

Acknowledgment. -- This work was carried out under contract N8onr-74300 with the Office of Naval Research whose support is gratefully acknowledged.

FIGURE 4

HEATS OF DESORPTION
BENTONITE — WATER AT 25° C.
(BENTONITE ACTIVATED AT 100°C., 48 HRS.)



DISTRIBUTION LIST FOR TECHNICAL REPORTS

Lehigh Univ. - HETEROGENEITY OF SURFACES - N8onr-74300 - NR 358-186

No. of Copies

Addressee

1	Commanding Officer Office of Naval Research Branch Office The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois
2	Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York
1	Commanding Officer Office of Naval Research Branch Office 1030 E. Green Street Pasadena 1, California
2	Commanding Officer Office of Naval Research Branch Office Navy #100 Fleet Post Office New York, New York
6	Director Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer
2	Chief of Naval Research Washington 25, D. C. Attn: Code 425
1	Technical Library OASD (R and D) Pentagon Room 3E1065 Washington 25, D. C.
1	Technical Director Research and Development Division Office of the Quartermaster General Department of the Army Washington 25, D. C.
1	Research Director Chemical and Plastics Division Quartermaster Research and Development Command Natick, Massachusetts

DISTRIBUTION LIST FOR TECHNICAL REPORTS-page 2

Lehigh Univ. - HETEROGENEITY OF SURFACES - N8onr-74300 - NR 358-186

<u>No. of Copies</u>	<u>Addressee</u>
1	Scientific Director Quartermaster Research and Development Command Natick, Massachusetts
1	Director Office of Scientific Research Air Research and Development Command P. O. Box 1395 Baltimore 3, Maryland
1	Office of the Chief of Ordnance Department of the Army Washington 25, D. C. Attn: ORDTB-PS
1	Office of Chief of Staff (R and D) Department of the Army Pentagon 3B516 Washington 25, D. C. Attn: Chemical Advisor
2	Director, Naval Research Laboratory Washington 25, D. C. Attn: Chemistry Division
1	Code 6170
2	Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 331
2	Chief, Bureau of Aeronautics Department of the Navy Washington 25, D. C. Attn: Code TD-4
2	Chief, Bureau of Ordnance Department of the Navy Washington 25, D. C. Attn: Code Ad-3
5	ASTIA Document Service Center Knott Building Dayton 2, Ohio

DISTRIBUTION LIST FOR TECHNICAL REPORTS-page 3

Lehigh Univ. - HETEROGENEITY OF SURFACES - N8onr-74300 - NR 358-186

<u>No. of Copies</u>	<u>Addressee</u>
1	Director of Research Signal Corps Eng. Laboratories Fort Monmouth, New Jersey
1	U. S. Naval Radiological Defense Lab. San Francisco 24, California Attn: Technical Library
1	Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Division
1	Office of Ordnance Research 2127 Myrtle Drive Durham, North Carolina
1	Technical Command Chemical Corps Chemical Center, Maryland
1	Brookhaven National Laboratory Chemistry Division Upton, New York
1	Atomic Energy Commission Research Division, Chemistry Branch Washington 25, D. C.
1	Atomic Energy Commission Library Branch Technical Information ORE Post Office Box E Oak Ridge, Tennessee
1	Office of Technical Services Department of Commerce Washington 25, D. C.
1	Dr. M. A. Cook Department of Chemistry University of Utah Salt Lake City, Utah
1	Superintendent, Industrial Test Lab. Philadelphia Navy Shipyard Philadelphia 12, Pennsylvania Attn: Development Branch

DISTRIBUTION LIST FOR TECHNICAL REPORTS-page 4

Lehigh Univ. - HETEROGENEITY OF SURFACES - N8onr-74300 - NR 358-186

<u>No. of Copies</u>	<u>Addressee</u>
1	ONR Resident Representative University of Pennsylvania Room 213 Hare Building Philadelphia 4, Pennsylvania
1	Consolidated Vultee Aircraft Corp. San Diego 12, California Attn: Engineering Library
1	Dr. N. Hackerman Department of Chemistry University of Texas Austin, Texas
1	Dr. Conway Pierce Department of Chemistry Pomona College Claremont, California
1	Dr. P. H. Emmett Department of Chemical Engineering Johns Hopkins University Baltimore, Maryland
1	Dr. Ralph Beebe Department of Chemistry Amherst College Amherst, Massachusetts
1	Argonne National Laboratory Post Office Box 5207 Chicago 80, Illinois Attn: Director, Information Div.
1	Director, Naval Boiler and Turbine Lab. Philadelphia Naval Shipyard Philadelphia 12, Pennsylvania Attn: Mr. A. Howarth