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THE PROPERTIES OF ANODIC ALUMINUM OXIDES, II. A STUDY OF THE SURFACE ROUGHNESS

by

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ABSTRACT

A method for determining the ratio of true surface area to apparent surface area has been developed which may be applied to smooth metal foils of only 200 square centimeters apparent area. For rougher foils proportionately less may be used.

The method involves the adsorption of ethylene on the foil at -183°C . A new type of adsorption isotherm is found for most adsorbents.

The method promises to be useful in the study of the preparation of metal surfaces for optimum paint adhesion, in the study of conversion coatings for similar purposes and in the general study of corrosion phenomena.

Surfaces of anodized aluminum are found to be very rough. Their very large surfaces are consistent with the pore theory of anodic film structure and account for the excellent adhesion of paint to these surfaces.

THE PROPERTIES OF ANODIC ALUMINUM OXIDES, A STUDY OF THE SURFACE ROUGHNESS

INTRODUCTION

Authorization

1. This study was begun under authority of Bureau of Aeronautics Project Order No. 111/43 which was discontinued in June 1944. However, because of the fundamental relation to service problems of corrosion, it is now being continued under authority of the Office of Naval Research Project Order 49/46. The corresponding NRL problem number is 32C27-01.

Statement of the Problem

2. In the general investigation of anodic aluminum oxides and the role which they play in reducing corrosion, the first report, (13)*, was concerned with diffusion of electrolytes through membranes of anodic aluminum oxide. The subject now to be presented covers a second factor involved in the investigation of anodic aluminum oxides, namely, a method of measuring the true surface area, or roughness, of comparatively small metal specimens. This question of surface roughness arises in studies of conversion coatings of metals, such as the anodization of aluminum and the formation of phosphate coatings on steel. It also appears in the problem of the nature of adhesion of paint to such surfaces and to surfaces produced by other methods of surface treatment.

3. When Naval equipments and installations are protected by paints, corrosion is prevented as long as the paint remains undamaged and its adhesion to the underlying metal is good. The damage factor is one not readily controlled but there are two ways of reducing to a minimum the corrosion failures due to poor adhesion or loss of adhesion of protective coatings to metal surfaces.

4. Adhesion can be destroyed by corrosive materials passing through the paint film. These materials corrode the underlying metal and undermine the paint which then peels and lifts off to expose the metal to direct corrosive attack. This type of failure is best controlled by proper formulation of the protective coating material, i.e., by use of coatings which are least permeable to the corrosive materials.

5. If the metal surfaces are not properly treated before painting, the finest protective coating will be of little value. Adhesion to uncorroded metals is determined by both chemical and physical factors. Chemical forces of adhesion are not considered in this report. It suffices here to say that these are a function of the composition of the metal surface and of the protective coating. The total chemical and physical forces of attraction are for a

* Numbers in parentheses are used for references.

particular metal and coating equal to a constant multiplied by the area to which the coating is applied:

$$F = k \times A \quad (5.1)$$

Area in this equation is not the apparent area of the metal surface as determined by the gross dimensions of the surface but rather the true submicroscopic area. Therefore it is seen that for a given metal the force of adhesion between a protective coating and the metal is a function of the total true area per unit apparent area of the coated metal, a ratio called roughness factor or specific area.

6. It is the purpose of this report to describe a method for determining the magnitude of these true surface areas. It has also been an objective to show the relation of true surface area of aluminum to certain surface treatments.

Methods of Determining Surface Areas by Gas Adsorption

7. Of the many methods employed in the past for determining surface areas, most are clearly unsuitable for the present purpose. Procedures involving the adsorption of dyes from solution, for example, are undesirable because of the possibility of the action of solutions on metal surfaces. The only method which seems likely to be useful is that based upon the measurement of the adsorption of gases. This yields positive results and introduces the least possibility of surface change.

8. The first successful method of determining surface areas from adsorption isotherms was proposed by Brunauer and Emmett in 1935 (1). Their method, as originally put forward, was wholly empirical. It was later placed on a sound theoretical basis and has been extensively and successfully applied by the originators and by many others. The situation in regard to both theory and experiment up through 1941 has been admirably presented in Brunauer's monograph, "The Adsorption of Gases and Vapors" (2).

9. Most adsorption isotherms resemble that plotted in Figure 1 as type II. The moles of gas adsorbed are plotted against the relative pressure, P/P_0 , where P is the gas pressure and P_0 is the vapor pressure of the liquefied gas at the temperature of the adsorption run. The adsorption starts from zero pressure and rises rapidly with increasing pressure until a relative pressure of about 0.1 is reached. The slope of this isotherm then decreases rapidly and becomes constant. The straight-line section is terminated by a region of continuously increasing slope. At a relative pressure of 1 (the vapor pressure) the "adsorption" becomes indefinitely great as the gas liquefies. In Brunauer and Emmett's original procedure, it was assumed that "Point B" corresponds to the completion of a unimolecular layer of adsorbed gas. From the volume of the gas in the liquefied state, or from the crystal structure of the solidified gas, a reasonable estimate of the area occupied by a molecule of adsorbate (the gas adsorbed on the surface) may be made. Most measurements have involved the adsorption of nitrogen at the temperature of liquid nitrogen ($P_0 = 1 \text{ atm.}$). For the area of the nitrogen molecule, the value derived from the solid is 13.8×10^{-16} square centimeters; from the liquid, 16.2×10^{-16} square centimeters.

10. Certain other gases have also been used at their normal boiling points, for instance, oxygen, argon, carbon monoxide and butane (2, page 158). The saturation pressures in these examples are about one atmosphere. In addition, adsorption techniques have employed vapors at temperatures at which P_0 was considerably less than one

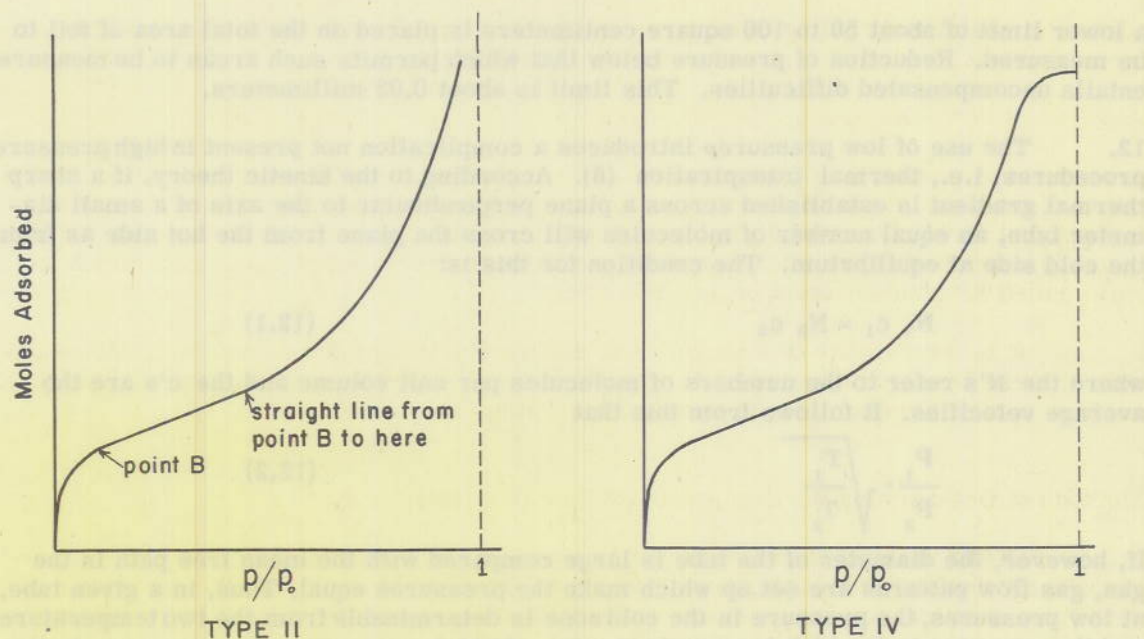


Figure 1 Typical Adsorption Isotherms, Moles Adsorbed Plotted Against the Relative Pressure

atmosphere. Livingston (3), for example, has employed for this purpose water, propyl alcohol and heptane. At still lower pressures, Beebe (4) has used krypton, -195.8°C (liquid nitrogen), $P_0 = 2$ mm. Wooten and Brown (5) employed ethylene at -183°C where its vapor pressure is about 0.036 mm. All of these appeared to be amenable to the Brunauer and Emmett surface area technique. Wooten and Brown used 17.55×10^{-16} square centimeters as the surface area of ethylene, a value derived from x-ray analysis of the crystalline solid.

11. The low pressure procedures are of particular interest when it is desired to measure small areas. In measuring an adsorption, a known quantity of gas is admitted into the system containing the adsorbent. From the known dead space and the measured pressure, the quantity of gas contained in the dead space, can be computed and by subtracting this from the quantity originally admitted, the amount of gas adsorbed may be calculated. To obtain measurements of any accuracy the amount adsorbed should be at least as great as that in the dead space. For gases which boil at liquid air temperatures, the correction to the ideal gas laws is not very accurately known and may approach 5 percent. Thus using nitrogen gas, there is a lower limit to the ratio of surface area to weight of sample beyond which accurate results are impossible. Brunauer (2, p. 298) places this limit at 0.2 square meter per gram. As the saturation pressure is reduced, the dead space correction decreases and, as long as the pressure can be measured to the same percentage accuracy, the least measurable area falls linearly with pressure. The lower relative accuracy of the McLeod gage reduces somewhat the relative advantage of low pressures. At some sufficiently low pressure, the limiting factor ceases to be the content of gas in the dead space and becomes instead the amount of gas adsorbed on the walls of the container. Since it is difficult to construct containers with an area of less than 50 square centimeters to hold unbent sections of foil of a total area of a few square centimeters,

a lower limit of about 50 to 100 square centimeters is placed on the total area of foil to be measured. Reduction of pressure below that which permits such areas to be measured entails uncompensated difficulties. This limit is about 0.02 millimeters.

12. The use of low pressures introduces a complication not present in high pressure procedures, i.e., thermal transpiration (6). According to the kinetic theory, if a sharp thermal gradient is established across a plane perpendicular to the axis of a small diameter tube, an equal number of molecules will cross the plane from the hot side as from the cold side at equilibrium. The condition for this is:

$$N_1 c_1 = N_2 c_2 \quad (12.1)$$

where the N's refer to the numbers of molecules per unit volume and the c's are the average velocities. It follows from this that

$$\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}} \quad (12.2)$$

If, however, the diameter of the tube is large compared with the mean free path in the gas, gas flow patterns are set up which make the pressures equal. Thus, in a given tube, at low pressures, the pressure in the cold zone is determinable from the two temperatures and the pressure in the high temperature zone. At high pressures, the pressures in the two zones are equal. There will exist a pressure region in which a transition occurs between these two types of behavior. This region occurs where the diameter of the tube equals the mean free path of the gas molecules. The pressure in the cold zone can then be found from that in the hot only by an empirical calibration of the tube. Furthermore, the pressure ratio is apt to vary erratically with slightly changing boundary conditions. For ethylene, the values of the mean free path at several pressures are:

Pressure	Mean Free Path
1.0 mm	2.3×10^{-3} cm
0.1 mm	2.3×10^{-2} cm
0.01 mm	0.23 cm
0.001 mm	2.3 cm

In carrying out the adsorption measurements described later in this report, provision was made to keep the diameter of the tube, connecting the adsorption bulb and manifold below the mean free path of ethylene at the operating pressure.

13. From kinetic considerations, the following equation valid for adsorption on a free surface, was derived by Brunauer, Emmett and Teller (2, p. 153, and 7):

$$\frac{P}{n(P_0 - P)} = \frac{1}{n_m c} + \frac{c - 1}{n_m c} \cdot \frac{P}{P_0} \quad (13.1)$$

P = Gas pressure

P₀ = Saturation pressure of the gas

n_m = Number of moles of gas required as adsorbate to cover the surface with a complete unimolecular layer

n = Total number of moles adsorbed

c = A quantity involving the temperature and heats of liquefaction and adsorption. This is constant for a gas on a given surface at one temperature.

By plotting the measured values of $P/n(P_0 - P)$ against the relative pressure, P/P_0 , a straight line is generally obtained. From the slope and intercept of this line, n_m and c may be computed. Usually the experimental data deviate upward from a straight line when P/P_0 exceeds about 0.3 to 0.4. The values of n_m as obtained by this method and by the older "Point B" method usually agree to better than 10 percent in the case of nitrogen adsorption on large areas (2, p. 157). In general, Brunauer and Emmett believe their method accurate to within 20 percent.

14. Brunauer (2, p. 154, and 8) has derived a relation which is valid for cases in which some factor limits the total number of layers of adsorbed gas to a value j .

$$n = \frac{n_m c x}{1 - x} \cdot \frac{1 - (j + 1)x^j + jx^{j+1}}{1 + (c - 1)x - cx^{j+1}} \quad (14.1)$$

Here, $x = P/P_0$ while c , n and n_m are defined as before. This equation does not allow for forces involved in capillary condensation. Somewhat similar considerations have been advanced by Foster (9). Brunauer's equation with $j = 2$ to 4 gives a long, nearly linear range which extends nearly to the point where $P/P_0 = 1$. Adsorption of a number of alcohols on silica gel gives isotherms of this type. Foster questions the identification of x with P/P_0 . In Brunauer's derivation this is a consequence of the assumption that the heat of adsorption of a molecule in any layer beyond the first is the same as the heat of condensation in the bulk liquid. This point was also taken by Livingston (3).

Anderson (10) has presented an equation which follows from the assumption that layers 3 through 9 involve smaller heats of adsorption than those of later layers. This equation is the same as the regular BET (Brunauer, Emmett, Teller) equation (13.1) with P_0 multiplied by a constant of the order of 1.4 to 1.5. Anderson reports that this modification in many cases extends the relative pressure range over which the equation is valid from the usual 0.05-0.3 range to a 0.05-0.7 range. The modification results in higher values of the calculated area by 4 to 19 percent.

15. In capillary condensation the last adsorbed layer in a capillary is attracted on both sides so that its heat of evaporation, like that of the first layer will be much greater than that of the other layers. The common isotherm for capillary adsorption is shown as type IV in Figure 1. This type of isotherm has been treated theoretically by Brunauer, Deming, Deming and Teller (2, p. 170 and 8). The course of the isotherm up to a value of P/P_0 of about 0.5 is the same as for the type II isotherms including a "Point B" and a straight portion. The total area (including that of the pore walls) may thus be found by either former method. Following a value of 0.4-0.5 for P/P_0 , the curve rises steeply as the capillaries fill with adsorbed gas. At a value for P/P_0 of approximately 0.9 the slope of the curve abruptly decreases as the capillaries become filled. The terminal value represents the volume of adsorbed gas required to fill the pores and permits the determination of the total pore volume (11). From the value of specific surface area and from that of specific pore volume, the average pore diameter and total pore length per unit volume of the adsorbent may be computed.

16. Harkins and Jura have recently published (12) another method of obtaining surface areas from adsorption isotherms. From thermodynamic considerations,

the following relation was derived:

$$\log (P/P_0) = B - \frac{A}{v^2} \quad (16.1)$$

P = pressure

P₀ = saturation pressure of the vapor at the temperature of the isotherm.

A, B = constants for a particular isotherm.

v = number of cubic centimeters (S.T.P.) of gas adsorbed.

The area, S, is given by:

$$S = k A^{1/2} \quad (16.2)$$

The constant, k, is always the same for a given gas at one temperature, but is variable with temperature. For nitrogen at its own boiling point the constant k is $4.06 \times 10^4 \text{ cm}^{-1}$. The constant, k, for a particular gas must be obtained by the use of one surface of known area. The equation predicts that, if $\log (P/P_0)$ be plotted against $1/v^2$ or any quantity proportional to it, such as $1/n^2$, a straight line will be obtained, the slope of which is -A. In general, agreement within 10-20 percent is obtained with the results of the Brunauer-Emmett-Teller Method (4,12).

Original Experiments Conducted in this Investigation

17. In this application of the technique, aluminum foil has served as the subject surface after first receiving certain surface treatments. Adsorption of ethylene gas at -183°C , (boiling point of oxygen) where its saturation pressure is of the order of .02 mm. Hg, has been adopted for this purpose. For comparison, the adsorption of nitrogen at -196°C , where its vapor pressure is about 760 millimeters, has been employed on some surfaces. To learn something of the lower limits of surface area determinable by this method, the surface areas of several glass bulbs were measured by the adsorption of ethylene. Finally, surfaces calculated by the "Point B" method with ethylene have been compared to applications of the Brunauer, Emmett and Teller equation (13.1) and the Harkins and Jura equation (16.1).

EXPERIMENTAL METHODS

Preparation of Surfaces for Adsorption Studies

18. The aluminum foil employed in this investigation was purchased from the J. T. Baker Chemical Co. Its thickness was about 28 microns and the purity as determined spectroscopically was about 99.5 percent. The impurity consisted chiefly of silicon and iron with some copper. This corresponds to the grade of aluminum generally used for commercial aluminum foil.

19. The foil was cleaned before use by swabbing with chloroform. It was further cleaned by treatment in a Soxhlet extractor with extraction naphtha. In certain cases the foil was then subjected to a 15-second dip at 86°C in a 5 percent solution of sodium carbonate (based on the anhydrous salt) followed by rinsing in distilled water. In certain other cases the foil was subjected to a two minute dip at 90°C into a solution containing 30 grams of chromium trioxide and 100 cubic centimeters of concentrated sulfuric acid in 900 cubic centimeters of water.

20. The anodization of aluminum foil was preceded by its solvent cleaning and sometimes by one of the subsequent dip treatments. The foil was anodized in a container of about three liters capacity provided with an electric stirrer and a lead cathode (for sulfuric acid) or an iron one (for chromic acid). Temperatures were held constant within $\pm 1/2^\circ\text{C}$. The general conditions of anodization are given in table I. The voltage was maintained at a fixed value in the case of chromic acid, whereas the current density was kept constant in the case of sulfuric acid. These conditions correspond to commercial practice.

TABLE I
ANODIZING CONDITIONS FOR ALUMINUM FOILS

Condition	Sulfuric Acid	Chromic Acid
Temperature	21°C	40°C
Concentration	15%*	10%†
Voltage	17	40
Induction Time ‡	15 secs. §	1 min. §
Current Density	15 ma/cm ²	6.5 ma/cm ² §

* Percent by weight of sulfuric acid.

† Percent by weight of chromium trioxide.

‡ Time required to reach operating voltage.

§ Approximate value.

21. The pretreatment, anodizing electrolyte, duration of anodization and thickness of the anodic layer are presented in table II for the various samples which were employed. The thickness was computed from the duration of the anodization by considerations developed in an investigation into the preparation of isolated anodic aluminum oxides (13).

22. Some studies were made of the adsorption of ethylene on the walls of glass bulbs of measured apparent area. In all except one case these bulbs were made from small commercial round bottom Pyrex flasks. These were cleaned in chromic acid cleaning solution and then with ethanol followed by nitric acid. Since it appears that treating glass with chromic acid cleaning solution roughens it somewhat (ca. 40 percent) (2, p. 322), one bulb was made by having the glassblower blow through a tube containing a drying agent (2, p. 327). Some studies were also made on porous glass from the same batch as that used by Emmett and DeWitt (11) and also Beebe (4). From nitrogen adsorption, the area was reported to be 120 square meters per gram. The piece of sheet which was furnished by Dr. Emmett was crushed in a hardened steel die and sieved, the 120-200 mesh portion being used.

23. The porous glass is presumably amorphous. The sulfuric acid anodic oxide film is amorphous and is composed of about 10-13 percent SO_3 , a few percent water and the rest alumina (13). Some of the other adsorbents which are amorphous are, pyrex glass and chromic acid anodized alumina. The latter has an average pore diameter of about 160 Angstrom units (14) and is composed of nearly pure amorphous alumina (13). The surface of the "sealed" foil (Foil A43) shows the electron-diffraction pattern of boehmite, $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (13). Surfaces of the aluminum foils of various pretreatments may well all have been covered with a thin layer of amorphous alumina, at most 60 Angstrom units thick (15).

TABLE II
DETAILS OF ALUMINUM FOIL SAMPLES STUDIED FOR SURFACE AREA

Surface	Apparent Area (Sq cm.)	Pretreatment (*)	Anodizing Electrolyte	Anodizing Time Min (Min)	Thickness of Anodic Film, (microns)
By Adsorption of Ethylene					
A1	90	none	----	----	----
A2	95.5	none	----	----	----
A4	12.5	†	----	----	----
A5	17.4	†	----	----	----
A6	95.5	‡	----	----	----
A7	96.2	‡	----	----	----
A42	25.4	none	H ₂ CrO ₄	42	5.5
A43	10.2	none	H ₂ CrO ₄	42	5.5
A44-47	14.2	‡	H ₂ CrO ₄	42	5.5
A48	11.0	none	H ₂ CrO ₄	22	2.8
A49	10.3	none	H ₂ CrO ₄	22	2.8
A50	25.3	none	H ₂ CrO ₄	11	1.4
A52	11.4	‡	H ₂ CrO ₄	42	5.5
A55	10.8	none	H ₂ SO ₄	15	6.3
A58	3.30	none	H ₂ SO ₄	30	12.5
A59-63	5.68	‡	H ₂ SO ₄	30	12.5
By Adsorption of Nitrogen					
A44-47	394	‡	H ₂ CrO ₄	42	5.5
A51-54	370	‡	H ₂ CrO ₄	42	5.5
A59-63	471	‡	H ₂ SO ₄	30	12.5

* The foil was initially solvent cleaned in all cases.

† Dipped for 15 seconds in 5% sodium carbonate solution at 86°C, followed by rinsing in distilled water.

‡ Immersed 2 minutes at 90°C in a solution containing 30 g of chromium trioxide and 100 cc. of concentrated sulfuric acid in 900 cc. of water.

Ethylene Adsorption

24. The apparatus employed in measuring the adsorption of ethylene at -183°C is shown in figures 2 and 3. It was developed from the one employed by Wooten and Brown (5). Where Wooten and Brown had used gold foil to trap mercury vapors, the trap E, cooled with dry ice-acetone mixture was employed in this research. By test, it was found that the insertion or removal of the cooling mixture produced a negligible effect upon the pressure in the system at pressures of 0.04 millimeters and less. The other main change was the addition of the magnet-operated plunger F of figure 2, which is shown in greater detail in figure 4. This was inserted at the liquid-oxygen level between

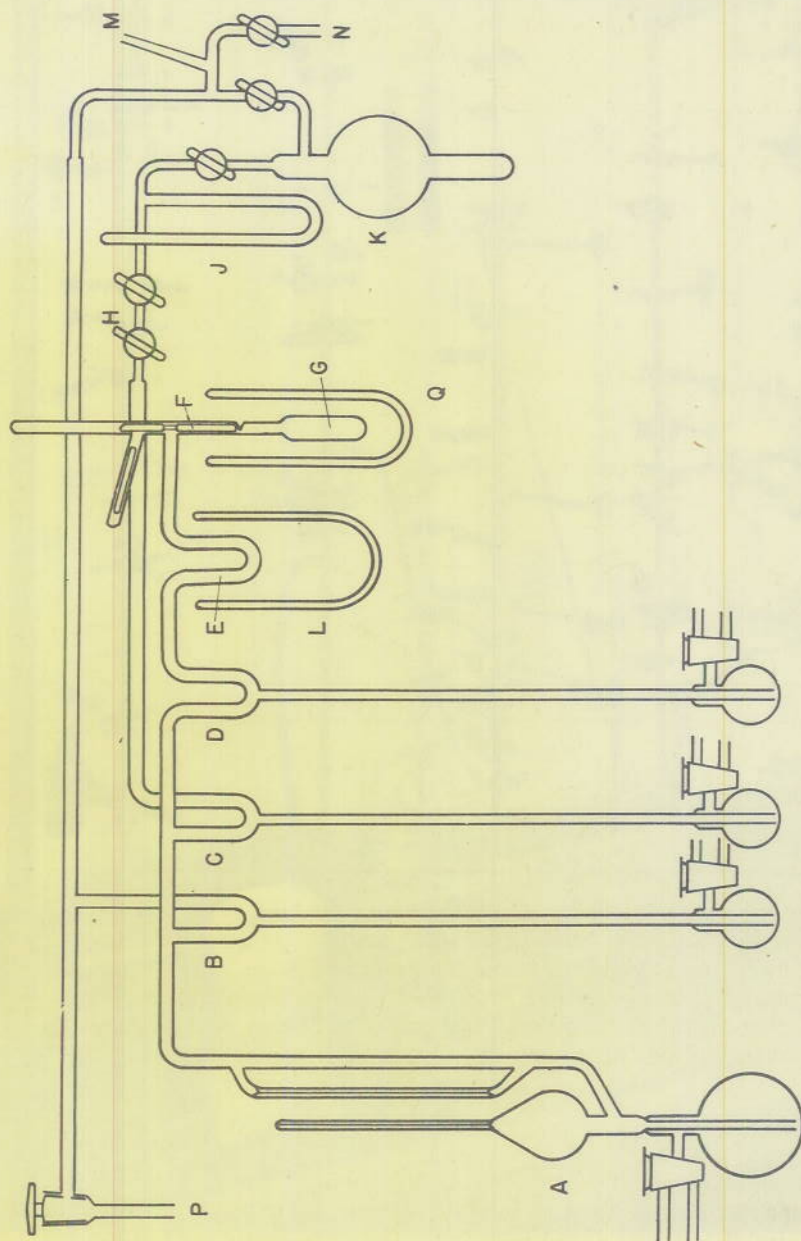


Figure 2 Apparatus for the Adsorption of Ethylene.

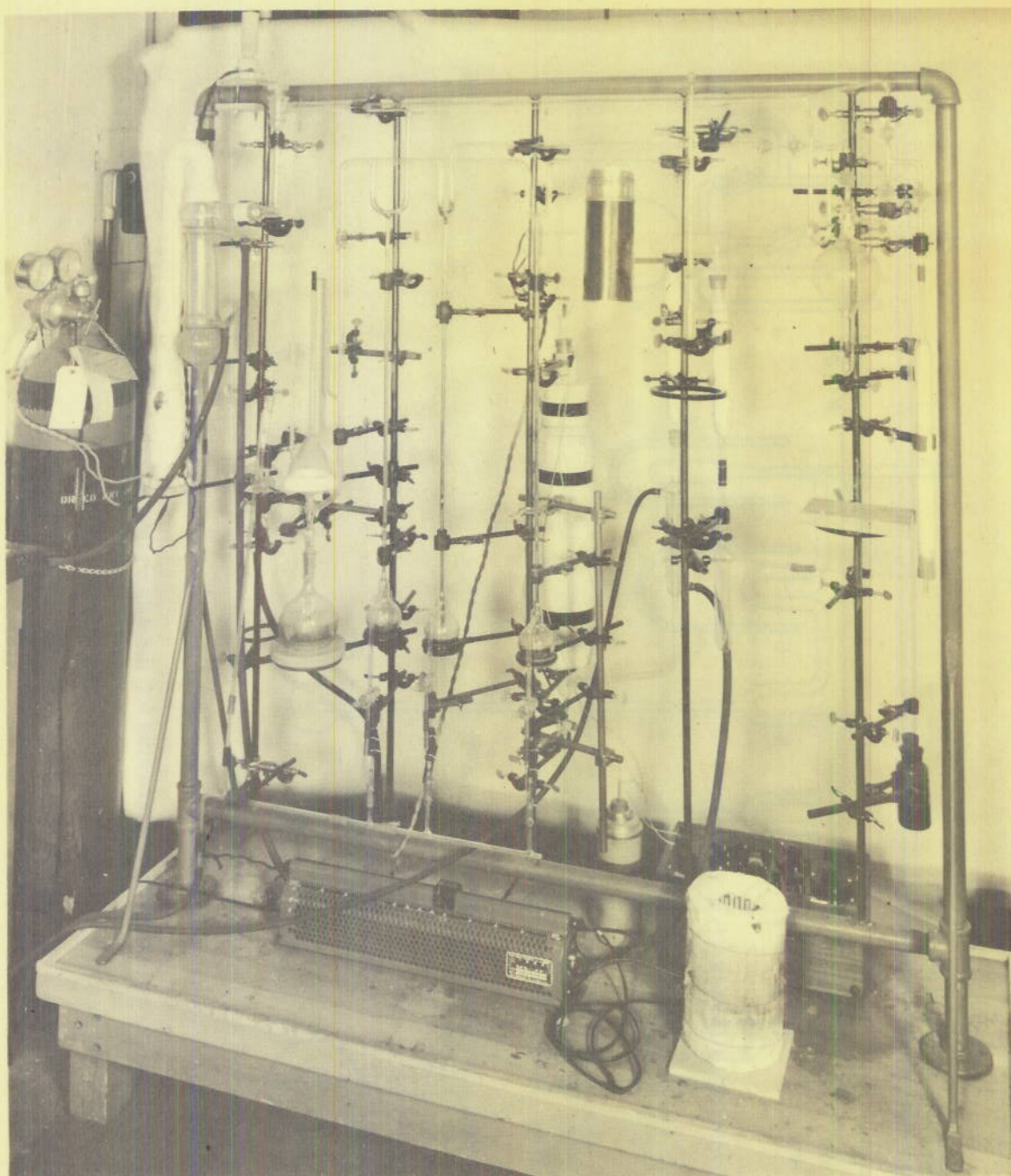


Figure 3 Photograph of Experimental Arrangement for Measuring the Adsorption of Ethylene

the adsorption bulb G and the remainder of the adsorption system. When the plunger was raised, fast pumping was possible. In the lower position the plunger provided a small tube to produce thermal transpiration discussed in paragraph 12. The plunger was raised above stop Z by means of a powerful horseshoe magnet operating upon the upper portion of the plunger into which iron filings had been sealed. Stop Z, consisting of an iron rod sealed into a glass tube, was then moved into the position shown in figure 4. Both the outer tube and the plunger were chosen for circularity and constancy of cross-section. The distance between the outer surface of the plunger tube and the inner surface of outer tube was 0.4 millimeters. The plunger was centered in its housing by two sets of four bulges which were blown in the plunger tube and then ground to proper dimensions and polished. The plunger was raised during pumping and at pressures below 2.5 microns. Experimentally, the lowering of the plunger first results in different readings at about 5 microns. Thus fast pumping was possible and equilibrium could be reached with reasonable rapidity at any pressure. At the higher pressures the characteristic effect of a small-radius tube resulted and this permitted the use of the square root law of paragraph 12 and the continuation of isotherms to higher pressures. Slight irreproducibility of the value of the saturation pressure and a drift in its value indicates that the transition pressure range was being entered at the highest pressures and that slightly smaller clearances might prove desirable.

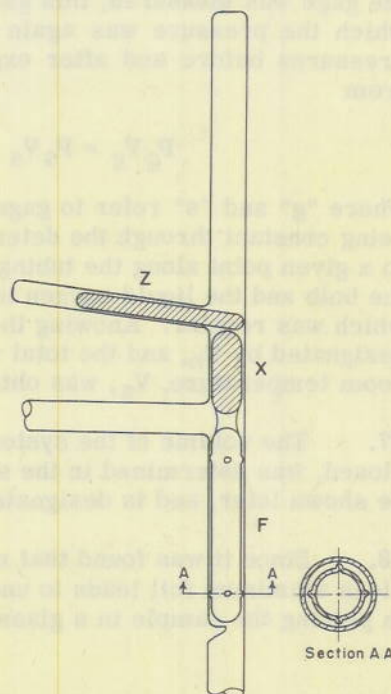


Figure 4 Magnetically Operated Plunger

25. Ethylene was prepared by passing ethanol over alumina at 375°C. The effluent ethylene was passed through a dry ice trap and collected in the storage bulb K (figure 2). By condensing the ethylene and pumping, allowing it to volatilize, recondensing and pumping for several cycles, permanent gases were removed. Samples were admitted to the system by the pair of gas-lock stopcocks H. The amount admitted in one operation was controlled by adjusting the pressure in the storage system which contained a manometer. In filling the subsidiary storage system the entire supply of ethylene was condensed and then after pumping, allowed to volatilize until the desired pressure was reached. This procedure reduced the quantity of higher boiling materials (diethyl ether) in the gas phase. It is believed that these procedures produced very pure ethylene.

26. For calculating the amount of gas adsorbed by a given sample, it was necessary to know the volumes of the portions of the system at room temperature and at liquid oxygen temperature. The volume of the portion of the system at liquid oxygen temperature must of course be determined with the metal or foil sample present in the system. In the case of the foils studied here, the volume of the sample was negligible compared with the other volumes involved. The volume of the bulb in which the sample was enclosed was determined by filling the bulb with water from a burette. The bulb with the sample in it was then attached to the system. The total volume of the system was obtained as follows. An amount of gas was admitted to the system and the mercury in the McLeod gage was raised so that a portion of the gas was trapped in the bulb of the gage. The rest of the system was then pumped off to zero pressure. The boundaries of the system at the McLeod gage and at the mercury cutoffs are defined by markings on the glass, to

which the mercury levels were always adjusted. After the gas pressure in the bulb of the gage was measured, this gas was allowed to expand into the rest of the system, after which the pressure was again measured. Since the volume of the gage bulb and the pressures before and after expansion were known, the volume may be calculated from

$$P_g V_g = P_s V_s \quad (26.1)$$

where "g" and "s" refer to gage and system respectively, the temperature of course being constant through the determination. The liquid oxygen level was always adjusted to a given point along the tubing above the sample bulb, G. Volume of the tubing between the bulb and the liquid oxygen level was calculated from the geometry of the system, which was regular. Knowing then the volume of the system at liquid oxygen temperature, designated by V_h , and the total volume, designated by V_s , the volume of the system at room temperature, V_a , was obtained by difference.

27. The volume of the system to cutoff D including that of the gage, when D was closed, was determined in the same manner as V_s . This volume is necessary as will be shown later, and is designated V_d .

28. Since it was found that making glass seals with the torch in the neighborhood of clean aluminum foil leads to undesirable oxidation, the following procedure was employed in placing the sample in a glass bulb. The bulb was made of glass tubing of sufficient size to just encompass the foil. After a short neck had been sealed onto the bulb, it was cleaned with chromic acid cleaning solution followed by ethyl alcohol - nitric acid cleaning. After sealing the bulb to the system, the pressures resulting from the introduction of successive known quantities of ethylene to the system were measured. The bulb was cooled with liquid oxygen during this operation. The bulb was then removed from the system at a point below the magnetic plunger F, (figure 4), and cut with a hot-wire glass cutter at a point near the top of the bulb proper, point A, figure 5. This cut was as far above the top of the foil sample as possible. The foil was inserted and the two pieces of the bulb clamped in position as shown in the figure, with the two edges fitting together. Nitrogen was then passed through the bulb by means of a quartz tube (Q) until the air was flushed from the bulb. With the nitrogen still passing through the bulb the seal was made with a gas-oxygen flame, glass blowing being accomplished by pinching shut a short piece of rubber tubing (R) which was fitted over the neck of the bulb.

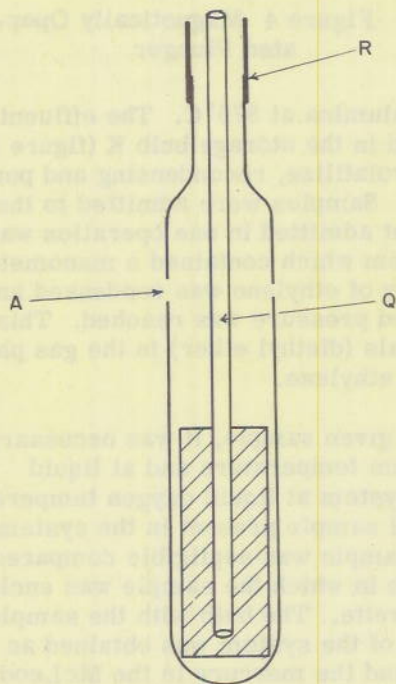


Figure 5 Method of Sealing Sample into Bulb

29. After the sample was in the system, it was pumped off. At first the samples were outgassed by heating to 350°C for one hour. It was later found sufficient merely to pump off the sample until negligible pressure was attained and maintained for a period of time equal to that required for determining the adsorption isotherm.

30. A small amount of gas was admitted to the system by means of stopcocks, H, (figure 2). The pressure was measured, and the bulb G (figure 2), containing the sample was then immersed in liquid oxygen. The pressure was measured until a constant value was reached. From these measurements the adsorption can be calculated as follows. It will be noted that the pressure P_2 in the adsorption bulb and tube at liquid oxygen temperature was different from the pressure, P_2 , in the remainder of the system at room temperature because of thermal transpiration.

$$\frac{P_2}{P_2'} = \sqrt{\frac{T}{T'}} \quad (30.1)$$

Where P_2 = pressure at gage when sample is in liquid oxygen.

P_2' = pressure in bulb at liquid oxygen temperature.

T = room temperature.

T' = temperature of liquid oxygen.

Then n , the moles of C_2H_4 adsorbed, is given by

$$n = \frac{P_1 V_S}{RT} - \frac{P_2 V_a}{RT} - \frac{P_2' V_b}{RT'} \quad (30.2)$$

Where P_1 = pressure when entire system is at room temperature, mm Hg.

V_S = total volume of system, liters.

R = gas constant, liter-mm Hg/mole-deg.

V_a = volume of part of system at room temperature in liters.

V_b = volume of part of system at liquid oxygen temperature in liters.

Then

$$n = \frac{P_1 V_S}{RT} - \frac{P_2 V_a}{RT} - \frac{P_2 V_b}{RT'} \sqrt{\frac{T'}{T}} \quad (30.3)$$

or

$$n = \frac{P_1 V_S}{RT} - \frac{P_2 V_a}{RT} - \frac{P_2 V_b}{RkT} \quad (30.4)$$

where

$$k = \sqrt{\frac{T'}{T}} \quad (30.5)$$

$$n = \frac{P_1 V_S}{RT} - P_2 \left[\frac{V_a}{RT} + \frac{V_b}{RkT} \right] \quad (30.6)$$

For each run this equation is of the form

$$n = AP_1 - BP_2 \quad (30.7)$$

where A and B are constants.

31. When the P_1 became too great to be measured by the McLeod gage, the following procedure was employed. With the sample bulb immersed in liquid oxygen, cutoff D was closed after a constant pressure had been obtained. Gas was then admitted to V_d (previously determined, paragraph 27) and the pressure measured. From the change in pressure in V_d the amount of gas admitted was

$$\Delta n = \frac{\Delta P V_d}{RT} \quad (31.1)$$

Cutoff D was then opened and the pressure again measured when equilibrium had been obtained. The total moles adsorbed, n , is now

$$n = \sum \left[\Delta n + \frac{P_1 V_s}{RT} - \frac{P_2 V_a}{RT} - \frac{P_2' V_b}{RT'} \right] \quad (31.2)$$

where P_1 is the last pressure reading before this procedure was initiated.

32. The moles of C_2H_4 adsorbed are plotted against the relative pressure P_2'/P_0 . The point B, where the curve begins to deviate from a straight line at the lower end, corresponds to the formation of a unimolecular film on the sample surface. This value of "n" multiplied by the area per mole of C_2H_4 gives the area of the sample.

33. The foregoing method for calculating the adsorption was used primarily for the glass bulbs. When foils were run, correction for adsorption by the glass container must be made. However, instead of determining separate isotherms for glass and sample, the following procedure was employed. The amount of gas in the system, given by

$$n = \frac{V_s P_1}{RT} \quad (33.1)$$

is plotted against the relative pressure when the sample bulb is immersed in liquid oxygen. The relative pressure is the pressure in the sample chamber divided by the saturation pressure of the gas obtained at the end of the run. This is done for glass alone and for glass plus the surface being studied. The difference in the amounts of gas required to produce a given relative pressure represents the amount adsorbed. These differences plotted against the relative pressure give the adsorption isotherm from which point B may be obtained as before.

34. Here again when the pressure in the system at room temperature becomes too great to be measured by the McLeod gage, the section V_d is used to admit measured amounts of gas to the system.

UNCLASSIFIED

Nitrogen Adsorption

35. Adsorption isotherms for nitrogen at liquid nitrogen temperature were determined for a few foils as checks on the low pressure work. The apparatus is shown in figure 6. In the nitrogen system a measured amount of gas was admitted from a gas burette and the pressure which resulted in the system was measured. From these data the isotherm can be calculated as shown in the following. Equilibrium at most pressures involved was readily obtained, and runs were less time consuming. The sample was sealed in the glass bulb in the same manner as described for the C_2H_4 studies. Tank nitrogen was used, purified by passing over copper turnings heated to $400^\circ C$.

36. Dead Space Determinations

"System" as used in the following discussion includes the capillary tubing from stopcock A to stopcock B, and to point G, and the sample bulb C. The liquid nitrogen level was always kept at a definite point H. The volume of the part of the system at room temperature, V_R , was first determined by sealing off the capillary tubing at H. After V_R was determined, a short piece of capillary was sealed on at H, to which sample bulbs could be attached. This sealing and reopening of the tubing at H gave no measurable change in V_R , as determined by sealing at H, measuring V_R , reopening and resealing at H and measuring V_R again.

37. Determination of V_R

The burette, D, was filled with nitrogen and, after its pressure had been adjusted to atmospheric by means of the small comparison manometer (F, figure 6), the volume of gas in the burette was read. The burette was a long 25-cc burette graduated in 0.05-cc intervals. It was calibrated with mercury and the corrections were found to be negligible (0.01 cc or less). Readings were ordinarily estimated to 0.005 cc. After the system had been evacuated and stopcock B closed, nitrogen was admitted to the system to a suitable pressure, P_2 , in the neighborhood of 760 millimeters. The stopcock connecting the burette to the system was closed, the burette pressure was adjusted to atmospheric as before and its volume read. Then, if the temperatures of the burette jacket and of the air are designated T_1 and T_2 ,

$$V_R = \frac{P_1 T_2}{P_2 T_1} \Delta V \quad (37.1)$$

With a sample bulb sealed to the system at H, the volume of the portion of the system at liquid nitrogen temperature V_n can be determined in a similar fashion. Nitrogen adsorption on the adsorbent was assumed to be zero at room temperatures.

38. Adsorption Isotherms

After the dead space had been determined, the system was pumped until a good vacuum could be maintained. The sample bulb was surrounded with liquid nitrogen and successive quantities of nitrogen admitted. Following each addition the pressure was determined. The moles of nitrogen adsorbed were calculated by the following equation:

$$n = \frac{P_1 \Delta V}{RT_1} - \frac{P_2 V_N}{RT_2(1 - \alpha P_2)} - \frac{P_2 V_R}{RT_2} \quad (38.1)$$

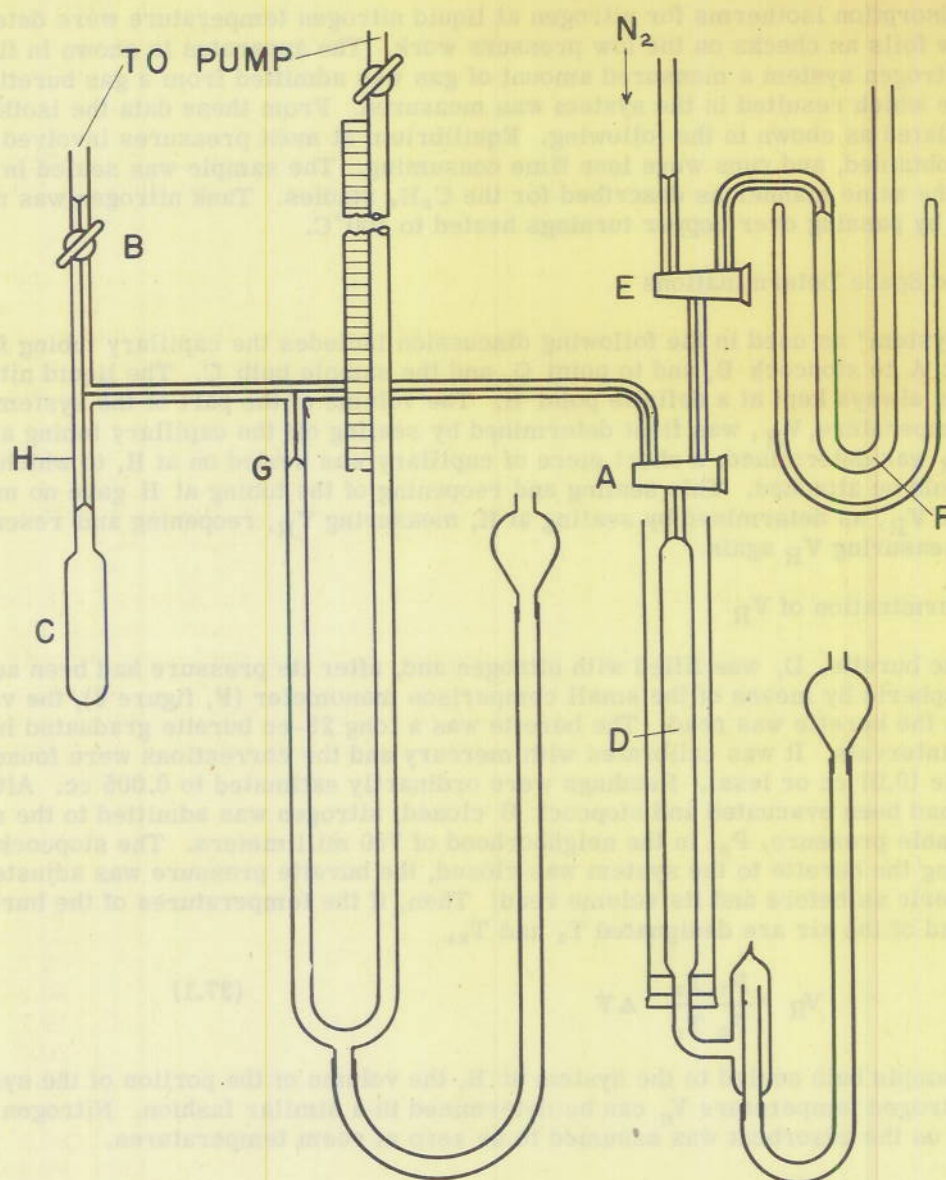


Figure 6 Apparatus for the Determinations of Surface Areas by Nitrogen Adsorption

The pressures are expressed in atmospheres and the constant, R , in liter-atmospheres per degree. The value, T_3 is the temperature of the liquid nitrogen bath, computed from the vapor pressure of liquid nitrogen which is found at the end of a run. When temperature and P_1 are constant throughout a run, the equation assumes the form:

$$n = a\Delta V - b P_2 - C P_2^2 \quad (38.2)$$

The correction factor, α , allows for the deviation of nitrogen vapor from ideal gas laws at the temperature of its normal boiling point. It is set equal to 0.039 by the formula given in reference (16).

39. For accurate results with this method, the portion of ΔV which represents adsorption should equal at least that portion representing the dead space. This consideration was satisfied in the runs on Foil A59-63 since this material had a much larger ratio of measured to apparent area and since a flattened sample tube was used to reduce the dead space.

DATA

40. The anodizing conditions for surfaces used in these experiments are described in table I. The individual history of each specimen is presented in table II.

41. The adsorption data are presented in graphical form in figures 7-28 inclusive. The gas introduced into the system and gas adsorbed are plotted against the relative pressure P/P_0 , where P is the pressure resulting from a particular amount of gas in the system and P_0 is the saturation pressure for ethylene at liquid oxygen temperature. This saturation pressure, determined at the end of each run by introducing an excess of ethylene, is recorded in table III for each adsorbent.

TABLE III
OBSERVED SATURATION PRESSURE FOR ETHYLENE

Surface	P_0 *	Surface	P_0 *
A1	20.9	A50	20.3
A2	20.3	A52	20.2
A4	20.7	A55	19.7
A5	21.1	A58	20.4
A6	20.3	A59-63	20.0
A7	20.4	A42 †	20.5
A42	20.9	A44-47 †	20.2
A43	21.6	Glass ‡	20.3
A44-47	21.9	Glass §	20.3
A48	20.3	Glass **	21.6
A49	21.2		

* Pressure in bulb expressed in microns.

† Sealed in water at 100°C.

‡ Freshly fused.

§ Freshly fused and then cleaned in chromic acid followed by ethyl alcohol and nitric acid.

** Porous Glass

The value of P_0 in these runs did not prove very reproducible. It was always found to be stable over a ten to twenty minute period, but exhibited a drift over longer periods. Values from 36.2 to 41.4 microns were observed at the McLeod gage corresponding to the pressures in the bulb recorded in table III. These values could not be correlated with barometric pressure which would affect the boiling point of oxygen and hence the temperature of the specimen bulb. Therefore, a series of measurements of the saturation pressure were made at several barometric pressures. From these, the experimental value at 760 millimeters was found to be 39.3 microns at the McLeod gage or 21.6 microns in the adsorption bulb.

42. The curves for ethylene on a glass bulb in figure 24, on porous glass in figure 25, and for nitrogen on aluminum foils in figures 26, 27, and 28 are corrected for "dead space" in the system and represent true adsorption isotherms. The other figures in this group present the adsorption curves as measured with no correction for "dead space" in the system.

TABLE IV
SURFACE AREAS FROM "POINT B" ON ETHYLENE ISOTHERMS

Surface	Point "B" moles $\times 10^7$	Calculated Area (Sq. cm.)	Apparent Area (Sq. cm.)	Roughness Factor
A1	1.57	167	90.0	1.86
A2	.99	105	95.5	1.10
A4	1.30	138	12.5	11.0
A5	1.29	137	17.4	7.9
A6	75.0	7970	95.5	83.5
A7	59.8	6360	96.2	66.1
A42	20.5	2180	25.4	86.0
A43	7.85	835	10.2	81.8
A44-47	11.05	1176	14.2	82.7
A48	3.7	393	11.0	35.7
A49	3.5	372	10.3	36.1
A50	4.7	500	25.3	19.7
A52	8.3	882	11.4	77.4
A55	24.9	2650	10.8	245.
A58	14.0	1484	3.30	450.
A59-63	33.0	3510	5.68	619.
A42 *	1.33	142	25.4	5.6
A44-47 *	3.9	415	14.2	29.2
Glass †	52.5	6490 **	----	113. ††
Glass ‡	1.0	106	120	----
Glass §	5.98	637	120	5.3

* Sealed by exposure to water vapor at 100°C for 30 minutes.

† Porous glass.

‡ Freshly fused glass bulb.

§ Glass bulb fused and then cleaned successively with chromic acid, ethyl alcohol and nitric acid.

** Calculated area for 5.75 mg. porous glass.

†† Area in sq. meters per gm.

Assuming a negligible volume occupied by the foil specimen, the difference between the adsorption curves for the bulb with and without its foil contents gives the true adsorption isotherm on the foil itself. These three curves are presented as "BF" for foil and bulb, "B" for bulb alone, and "F" for the true adsorption isotherm on the foil alone. In all cases, adsorption in moles of gas is plotted against the relative pressure. The best approximation of the completion of a unimolecular layer is indicated on each isotherm by the letter "b". The values of this factor for ethylene adsorption are tabulated in the second column of table IV and for nitrogen adsorption in the second column of table V.

43. In several runs on foils anodized in chromic acid the reversibility of these isothermal measurements was examined. After the maximum pressure was reached, successive portions of ethylene were removed and the adsorption-pressure equilibrium re-established. These values, obtained by reducing the pressure, fell on the isothermal curves obtained with increasing pressure. The adsorption was rapidly reversible and thus of a strictly physical type. This reversibility was not examined in the case of porous surfaces such as porous glass and foils A59-63. Therefore, the hysteresis effects observed by Emmett and DeWitt (11) were not observed.

TABLE V
SURFACE AREAS FROM "POINT B" ON NITROGEN ISOTHERMS

Surface	Point "B" moles $\times 10^5$	Calculated Area (sq. cm.)	Apparent Area (sq. cm.)	Roughness Factor
A44-47	4.20	41,300	394	105
A51-54	3.05	30,000	370	81
A59-63	31.5	310,000	471	653
A44-47 *	2.50	24,600	394	64
A44-47 †	4.65	45,700	394	116
Glass ‡	----	----	----	121

* Sealed in water at 100°C.

† Subjected to second sealing operation.

‡ Porous Glass.

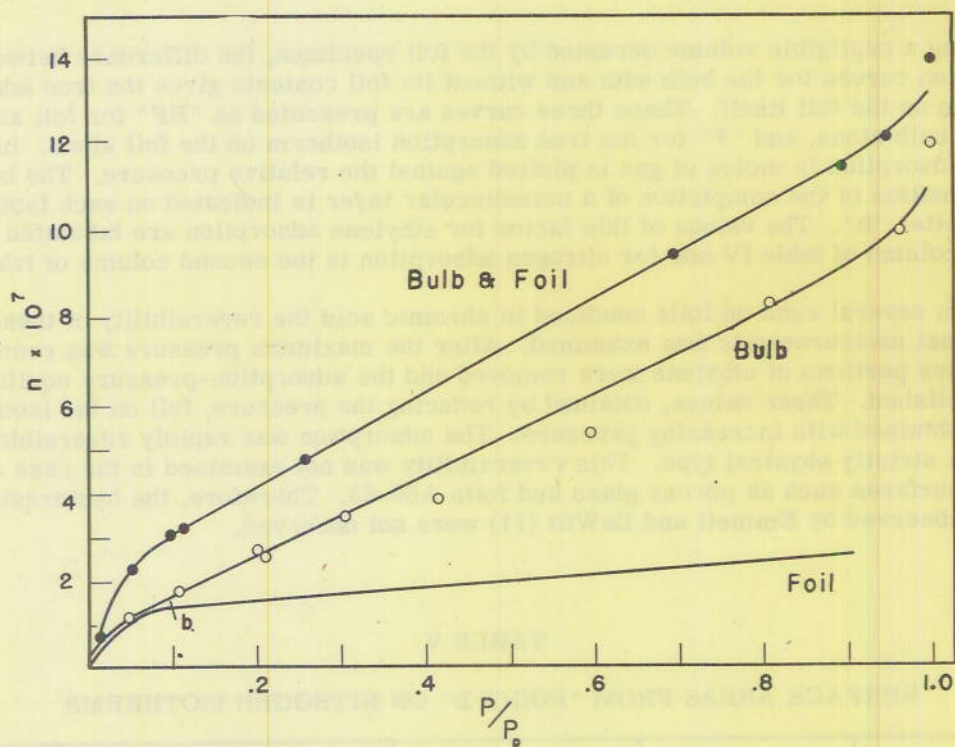


Figure 7 Adsorption of Ethylene on Untreated Aluminum Foil A1

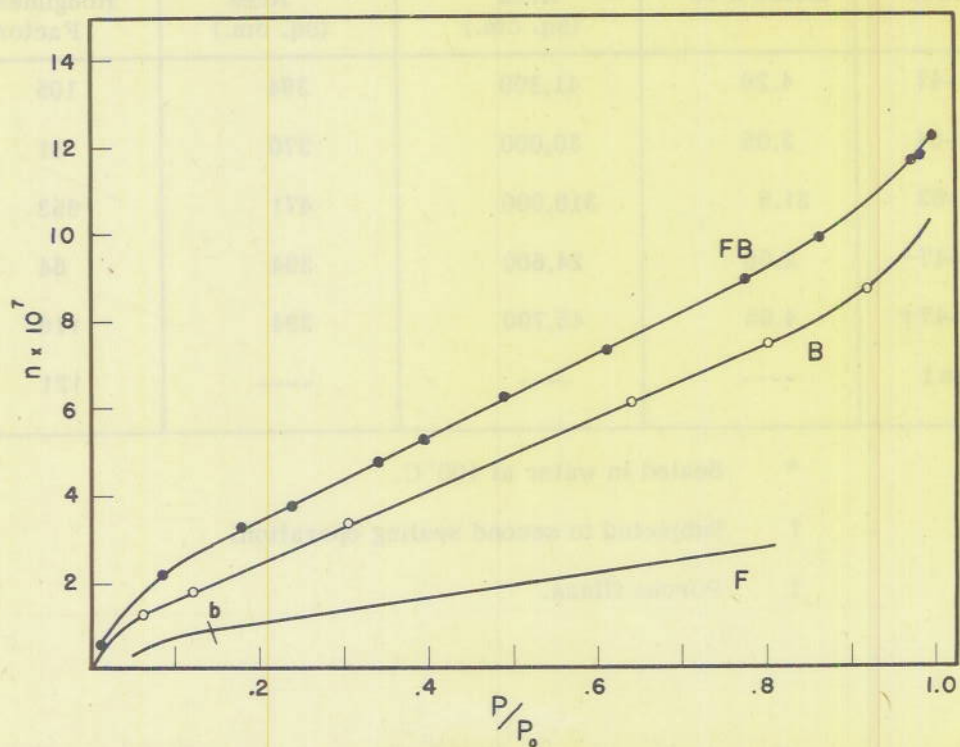


Figure 8 Adsorption of Ethylene on Untreated Aluminum Foil A2

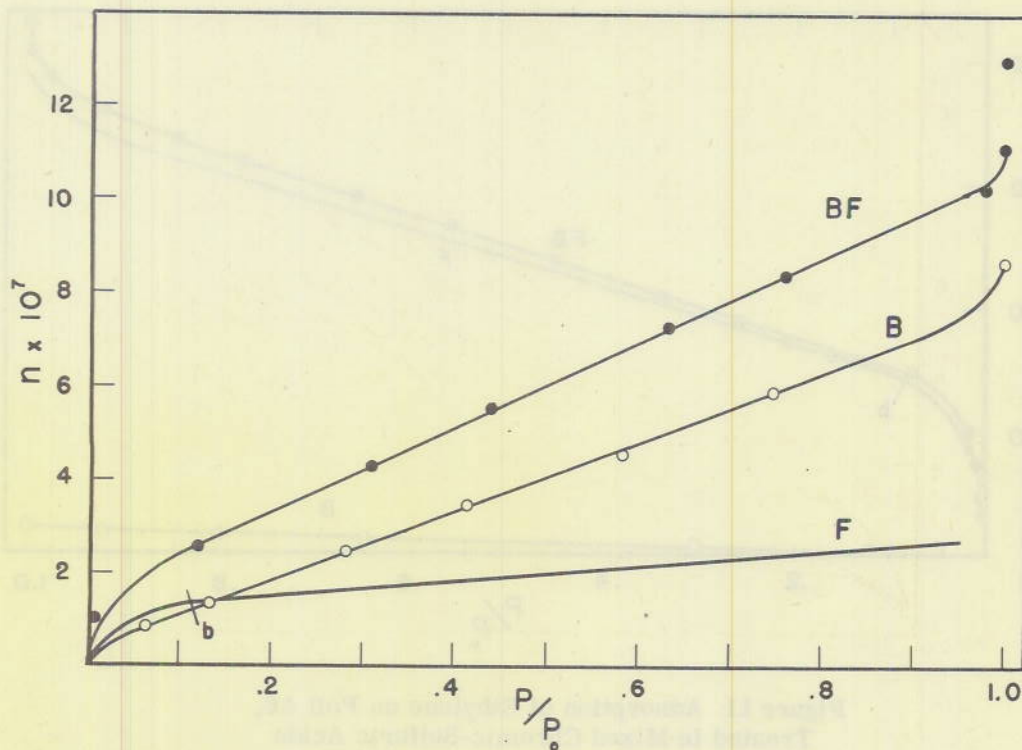


Figure 9 Adsorption of Ethylene on Foil A4, Treated with Sodium Carbonate

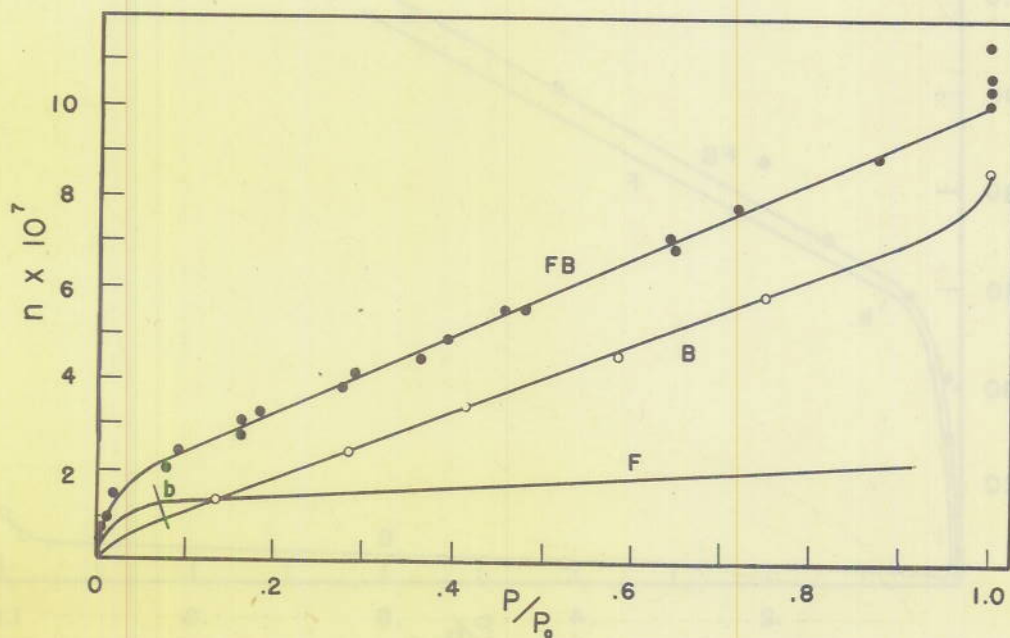


Figure 10 Adsorption of Ethylene on Foil A5, Treated with Sodium Carbonate

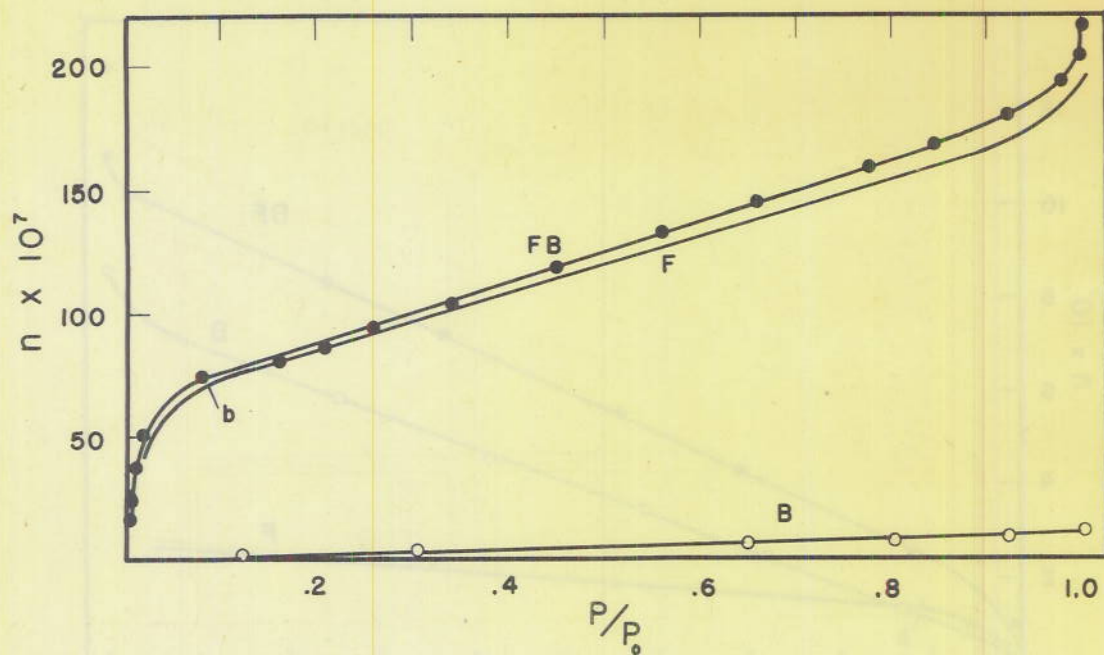


Figure 11 Adsorption of Ethylene on Foil A6,
Treated in Mixed Chromic-Sulfuric Acids

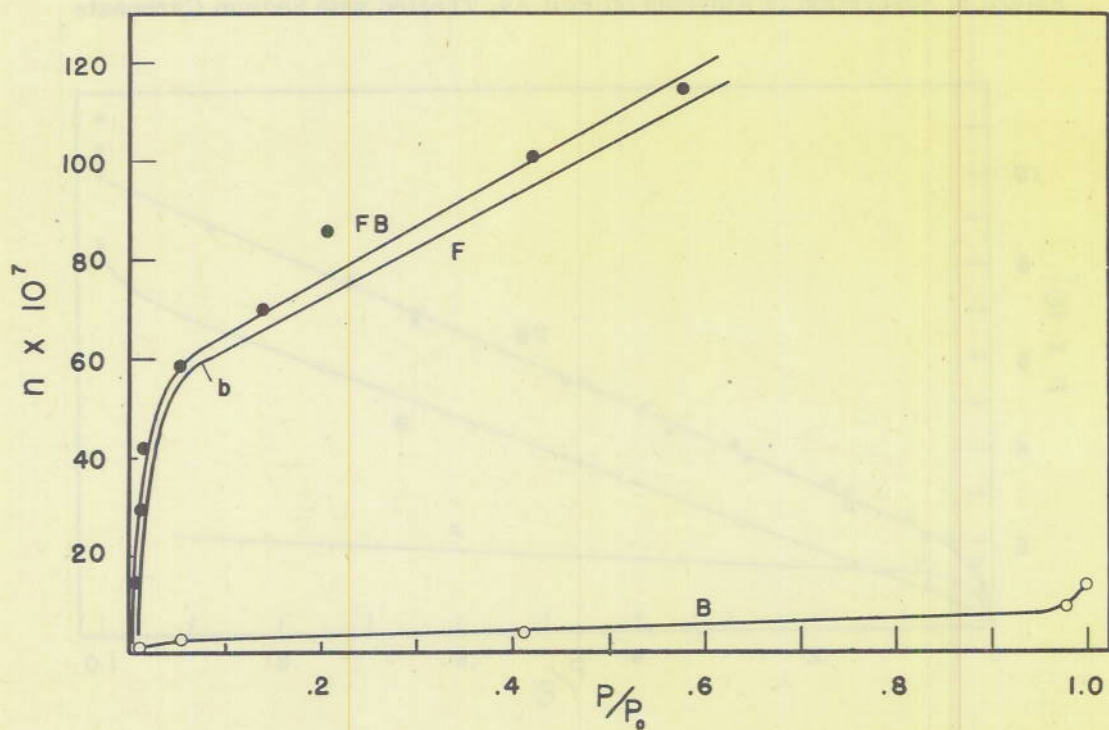


Figure 12 Adsorption of Ethylene on Foil A7,
Treated in Mixed Chromic-Sulfuric Acids

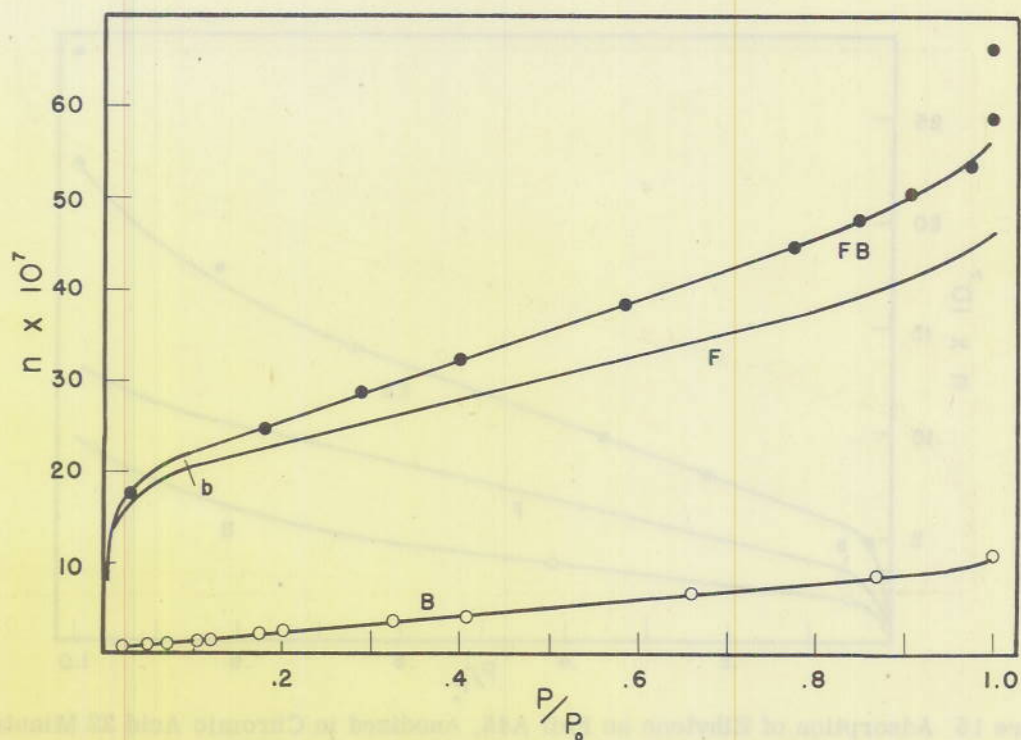


Figure 13 Adsorption of Ethylene on Foil A42, Anodized in Chromic Acid 42 Minutes

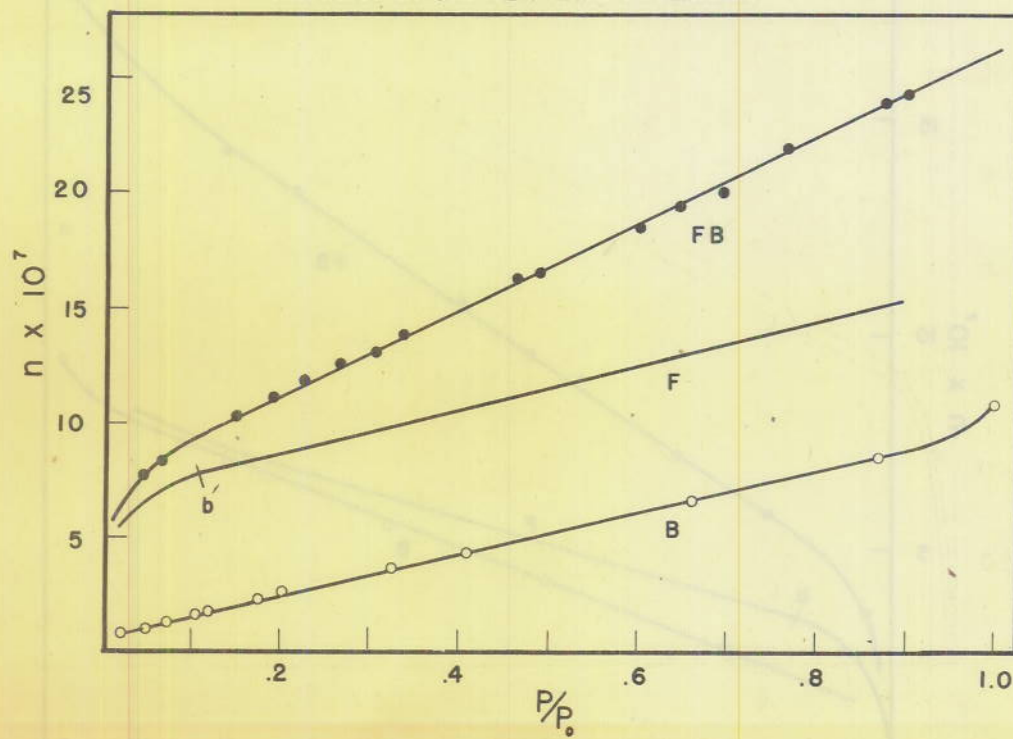


Figure 14 Adsorption of Ethylene on Foil A43, Anodized 42 Minutes in Chromic Acid

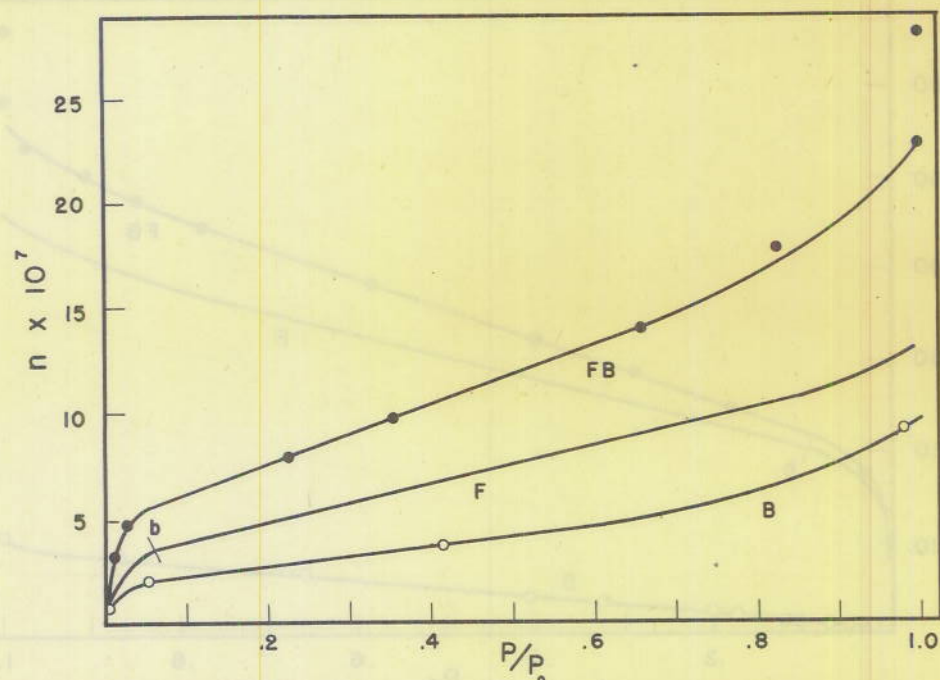


Figure 15 Adsorption of Ethylene on Foil A48, Anodized in Chromic Acid 22 Minutes.

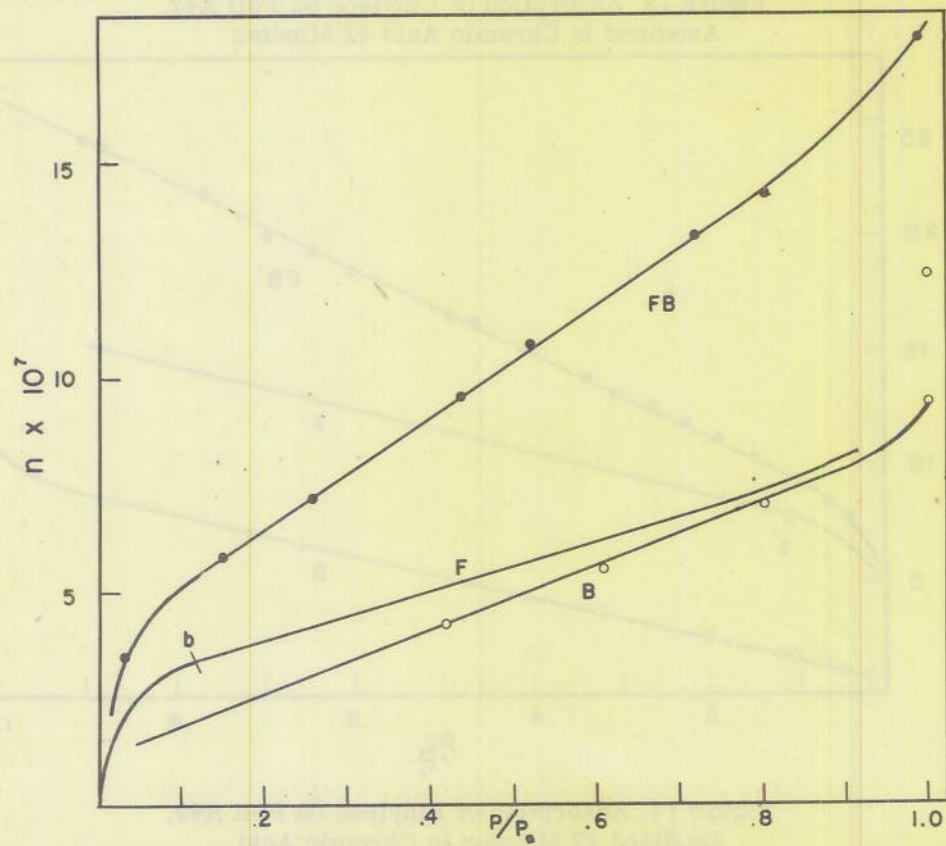


Figure 16 Adsorption of Ethylene on Foil A49, Anodized 22 Minutes in Chromic Acid.

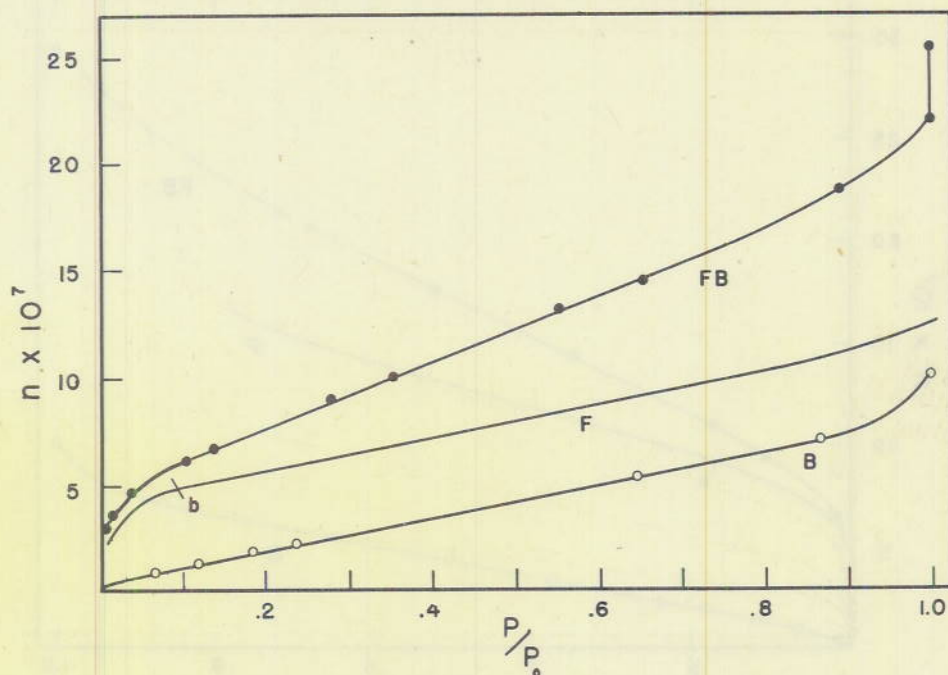


Figure 17 Adsorption of Ethylene on Foil A50,
Anodized 11 Minutes in Chromic Acid

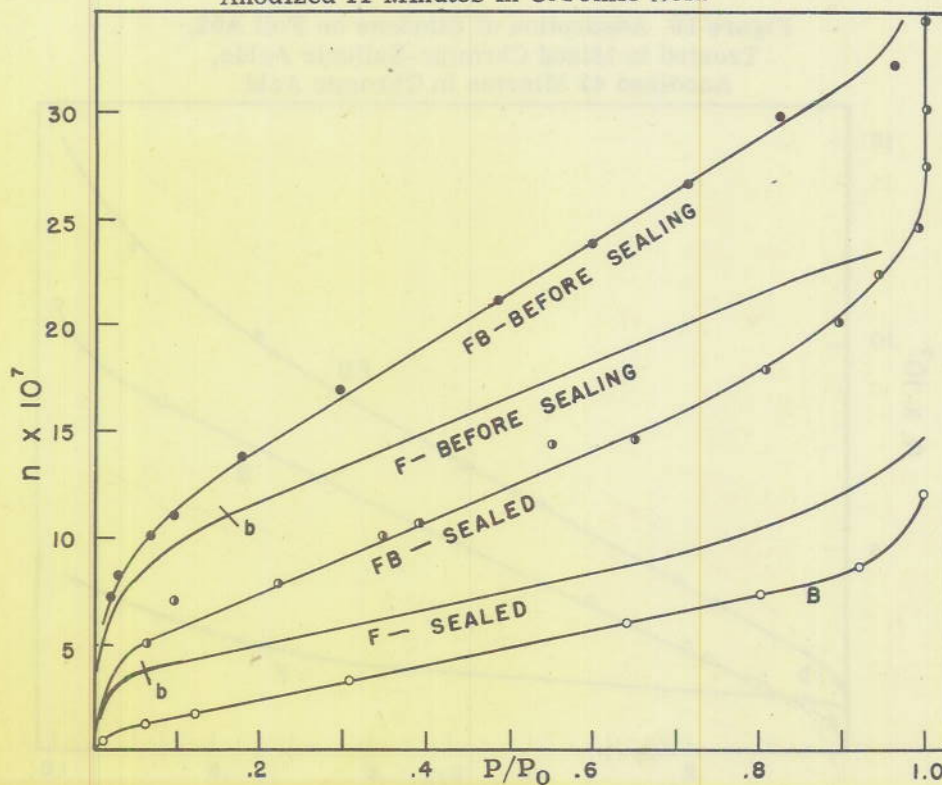


Figure 18 Adsorption of Ethylene on Foils A44-47,
Treated in Mixed Chromic-Sulfuric Acids,
Anodized 42 Minutes in Chromic Acid, and Sealed in Steam at 100 C.

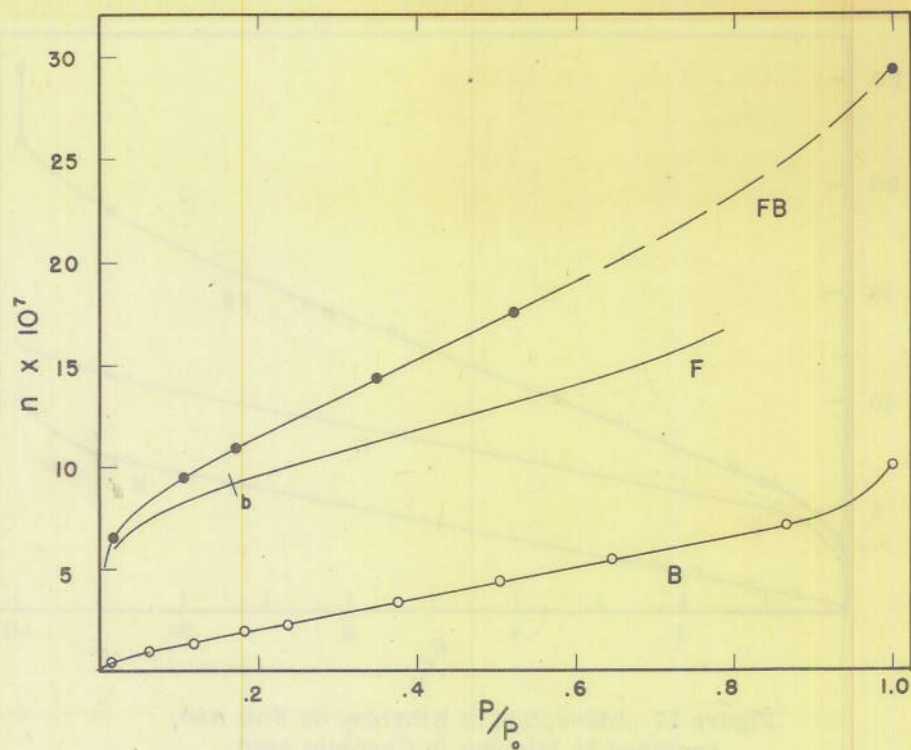


Figure 19 Adsorption of Ethylene on Foil A52,
Treated in Mixed Chromic-Sulfuric Acids,
Anodized 42 Minutes in Chromic Acid

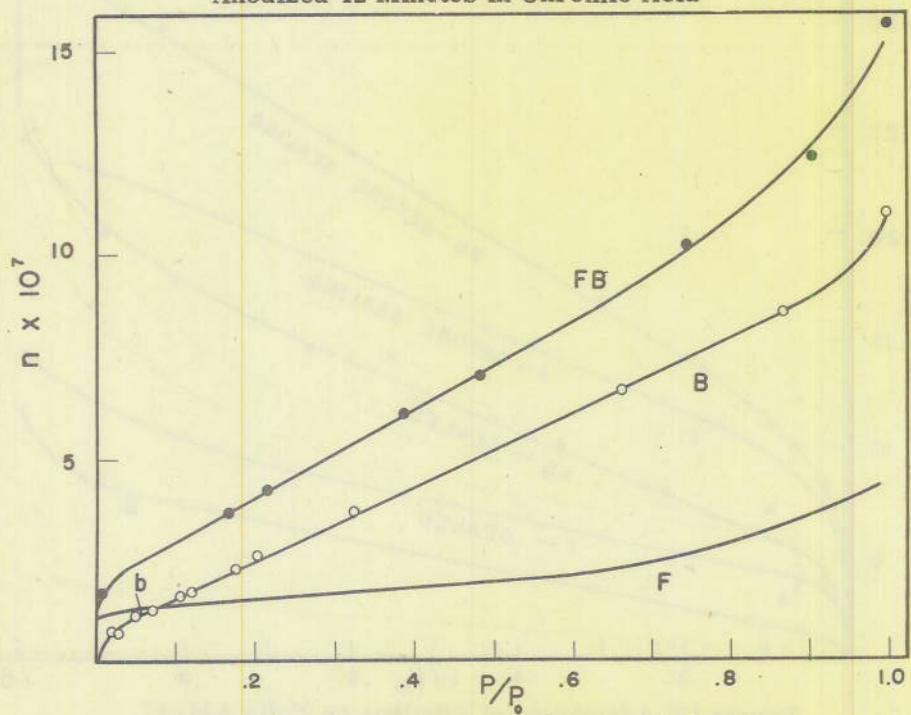


Figure 20 Adsorption of Ethylene on Foil A42,
Anodized 42 Minutes in Chromic Acid and Sealed in Steam at 100°C

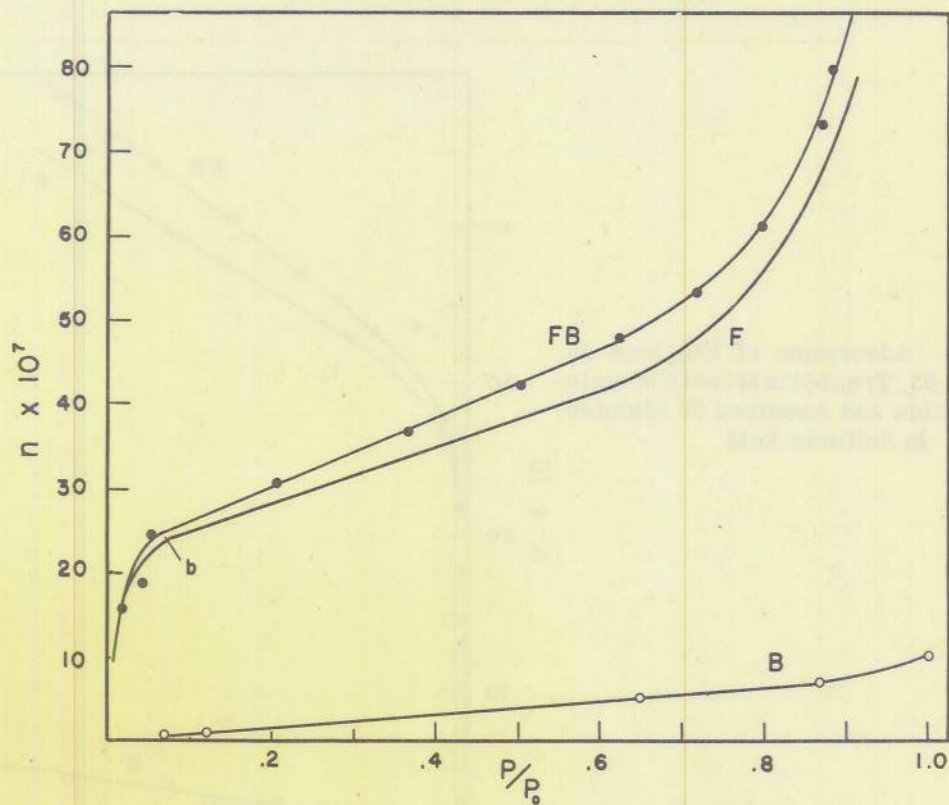


Figure 21 Adsorption of Ethylene on Foil A55,
Anodized 15 Minutes in Sulfuric Acid

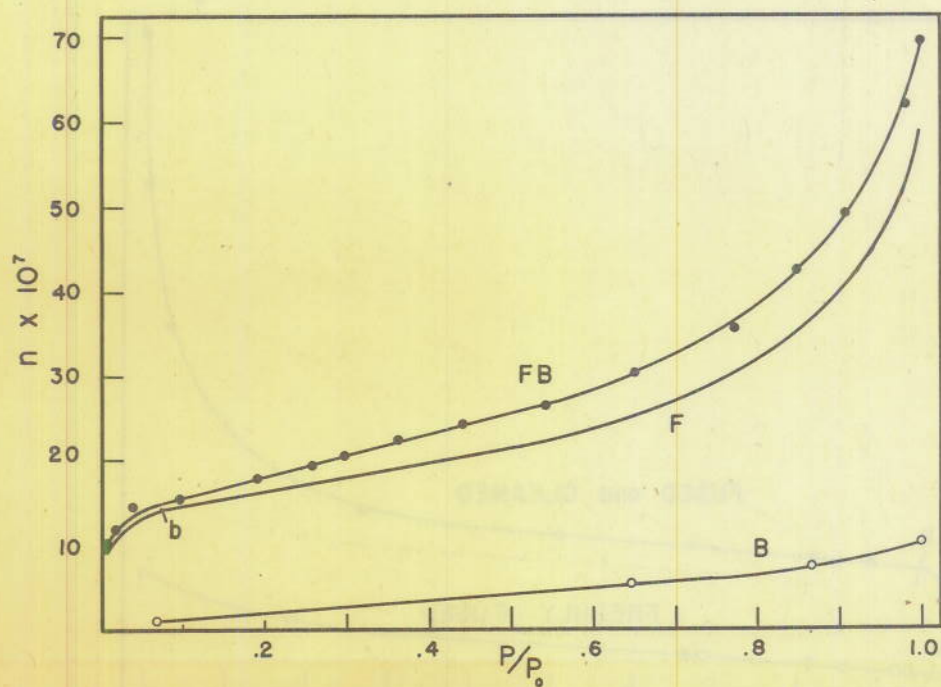


Figure 22 Adsorption of Ethylene on Foil A58,
Anodized 30 Minutes in Sulfuric Acid

Figure 23 Adsorption of Ethylene on Foils A59-63, Treated in Mixed Chromic-Sulfuric Acids and Anodized 30 Minutes in Sulfuric Acid

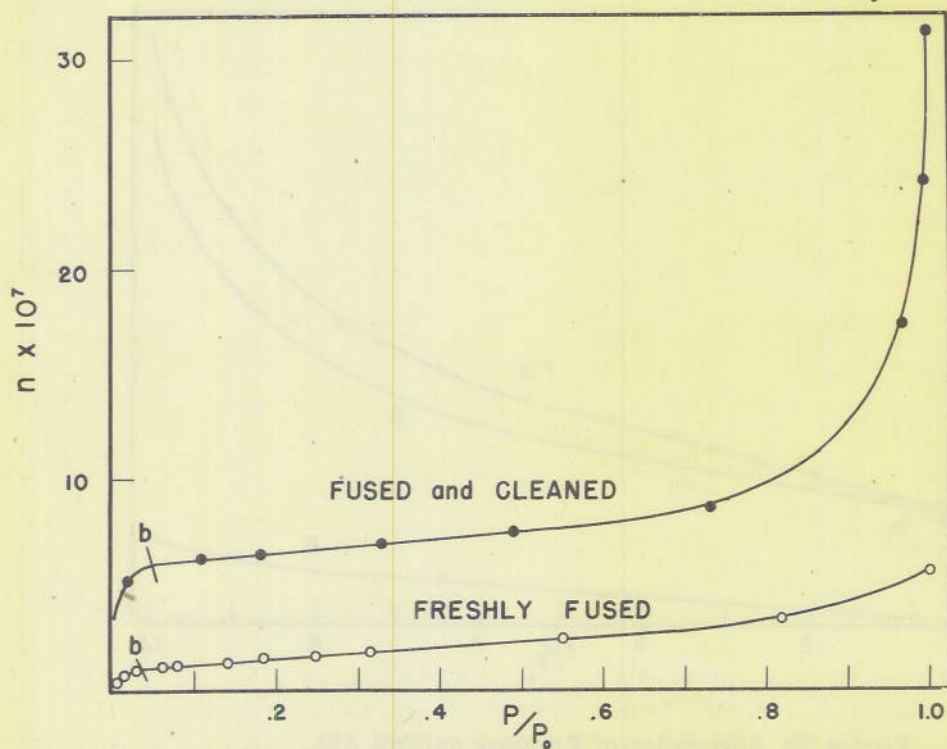
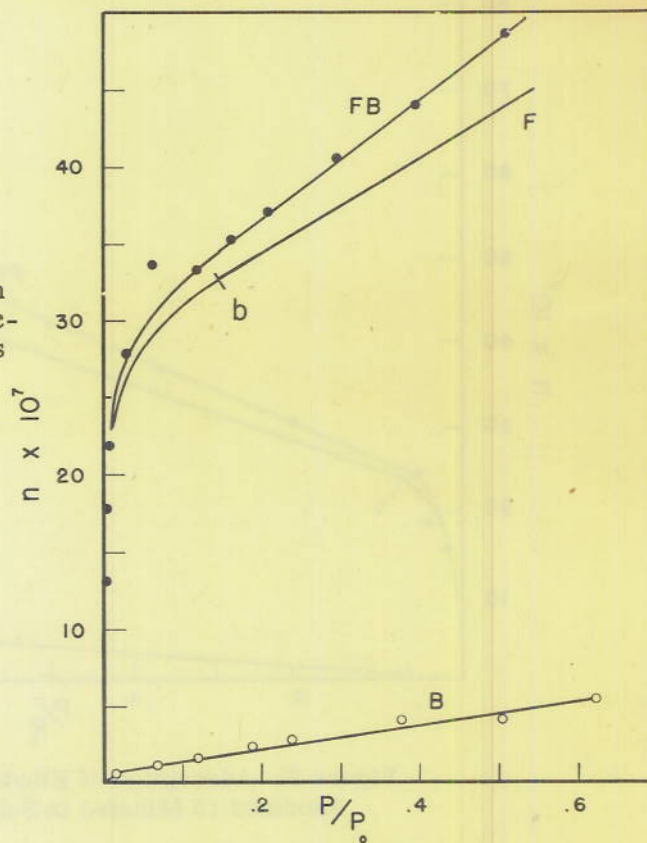


Figure 24 Adsorption of Ethylene on Glass Walls of Container Bulb

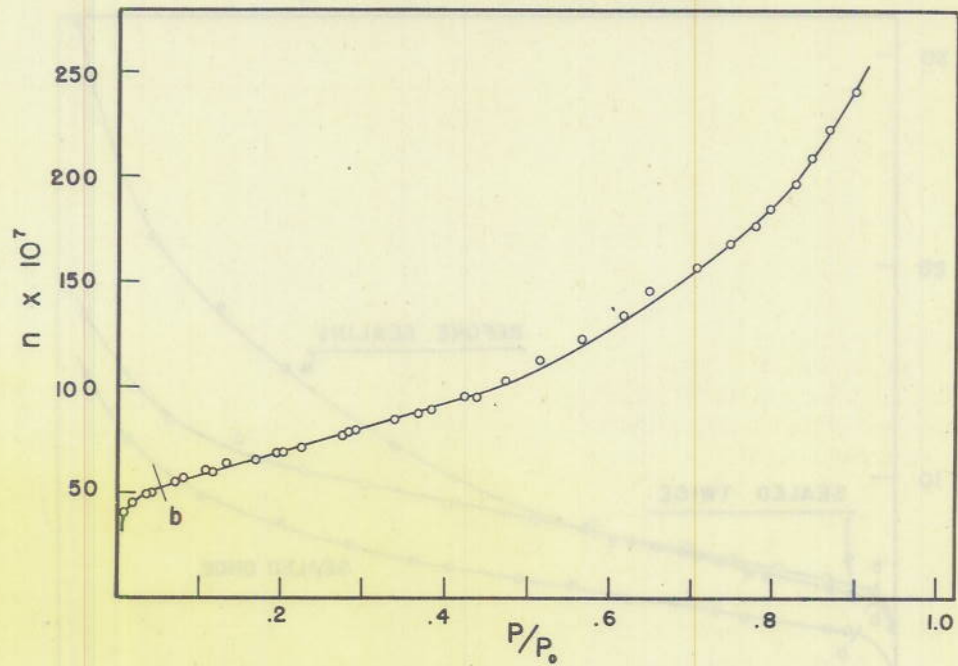
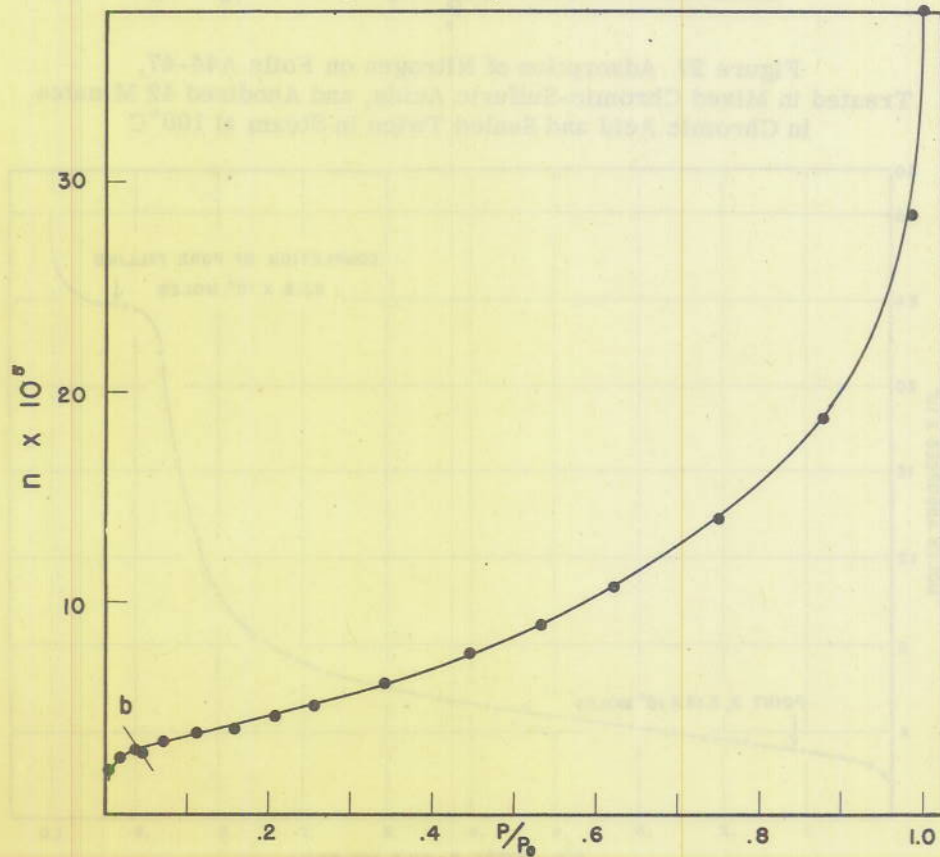


Figure 25 Adsorption of Ethylene on Porous Glass

Figure 26 Adsorption of Nitrogen on Foils A51-54,
Treated in Mixed Chromic-Sulfuric Acids and
Anodized 42 Minutes in Chromic Acid

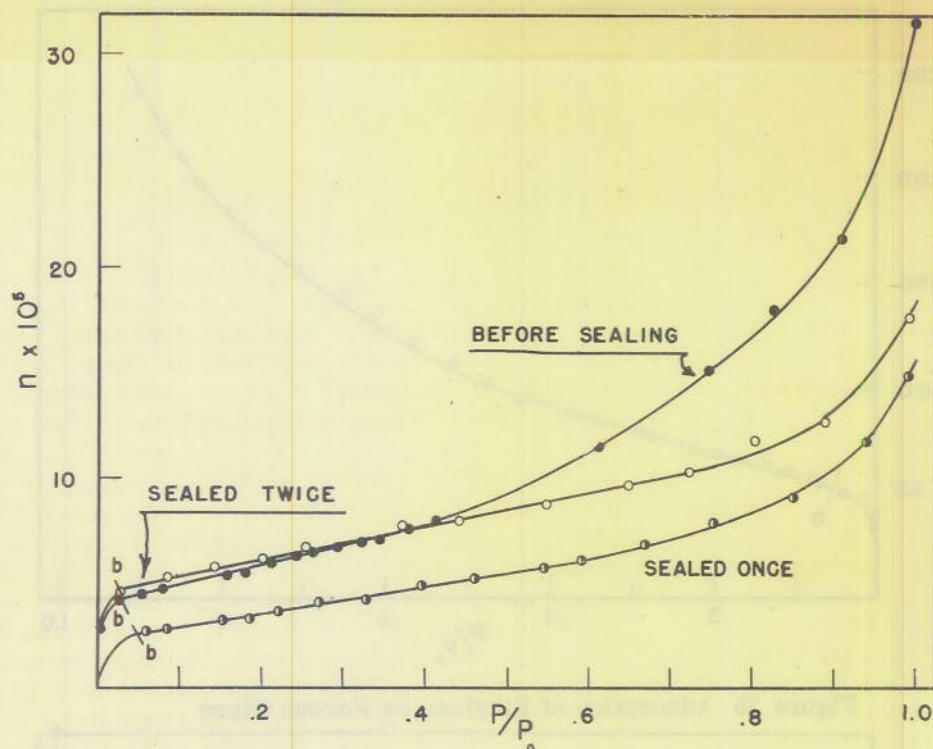


Figure 27 Adsorption of Nitrogen on Foils A44-47, Treated in Mixed Chromic-Sulfuric Acids, and Anodized 42 Minutes in Chromic Acid and Sealed Twice in Steam at 100°C

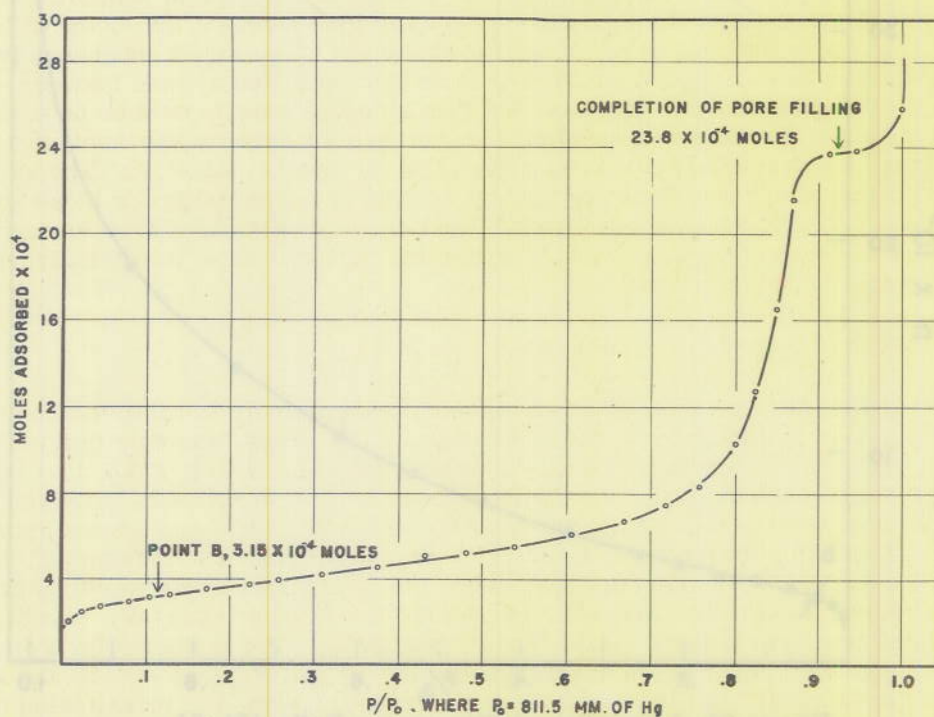


Figure 28 Adsorption of Nitrogen on Foils A59-63, Treated in Mixed Chromic-Sulfuric Acids, and Anodized 30 Minutes in Sulfuric Acid

EXPERIMENTAL RESULTS

Roughness Factors

44. Assuming the cross sectional area for the ethylene molecule to be 17.55×10^{-16} square centimeters, the area for each surface was calculated from the value of point "b" and was compared with the apparent area indicated by the gross dimensions of the specimens, to give the roughness factors. The term "roughness factor" used in this report to represent this ratio of measured area to apparent area, is designated as "F". These factors are presented for ethylene adsorptions in table IV and for nitrogen adsorptions in table V.

45. In a number of these measurements, the selection of point "b" on the curve was not very easily made. Ethylene on A59-63, figure 23, did not exhibit a sharp break at the completion of a unimolecular layer and furnishes a typical example of such a curve. In other cases, where the true area of the foil was small, the correction for "dead space" and for adsorption on the walls of the containing bulb was large and increased the magnitude of error in the area determination. Untreated Foils A1 and A2, figures 7 and 8, and the sealed oxide foils such as A42, figure 20, fell in this category. Attempts to measure the areas of Foils A43 and A49 after sealing were unsuccessful for this reason. In a number of the measurements, better accuracy could have been obtained by measuring more points in the region of point "b" but this improvement would be of small consequence, practically speaking, in these measurements.

46. An attempt was made to determine the surface area of a freshly fused glass bulb, figure 24, but the "dead space" correction was so large and errors in estimating the apparent area of the walls of the bulb were such as to give a roughness factor of less than 1. It is probable that this value is not far above one. The small roughness factor finds support in a number of runs on other bulbs which indicated a value between 1 and 1.1. Upon cleaning this bulb, its surface was then so rough that it could be determined with moderate ease. Surface measurements on untreated foils with apparent area below 100 square centimeters were not reproducible (Foil A1 and A2, table IV). The values obtained indicate a roughness factor of about 1.5. The reproducibility for those surfaces which had been roughened was much better. The values of calculated area for surfaces over 200 square centimeters are probably within the limits of experimental accuracy obtainable by this technique.

Types of Ethylene Adsorption Isotherms

47. Most of the ethylene adsorption isotherms do not directly fall into the classification of adsorption isotherms proposed by Brunauer (2). They resemble that portion of a type II, (figure 1) isotherm which lies between $P/P_0 = 0$ and $P/P_0 = 0.4$, that is, the straight line region extends to the saturation pressure. Two adsorbents, however, gave normal adsorption isotherms: aluminum anodized in sulfuric acid and porous glass, (figures 21, 22 and 25). Beyond a pressure of 9 microns in the first case and 11.5 microns in the second, the isotherms rose above the straight line with rapidly increasing slope. The region of high relative pressure was not investigated carefully enough to permit a distinction between type II and type IV isotherms. The isotherm for Foils A59-63, from evidence by nitrogen adsorption on A59-63 and ethylene on A55 and A58, is placed in the "normal" category in spite of the fact that it was not investigated beyond a pressure of 10 microns. Adsorptions on the walls of the glass bulbs were computed from data obtained on the empty bulbs. The isotherms definitely belong to the anomalous type and are typified in figure 24.

48. Upon plotting the adsorption data according to the BET method (equation 13.1), straight line regions were obtained in all cases. The straight line region extended from a relative pressure of about 0.03 to one of about 0.2 to 0.4. Typical examples of ethylene adsorption are presented in figures 29, 30, and 31.

49. Plots of the adsorption data according to the Harkins and Jura method (equation 16.1) produced straight line regions except for the foils anodized in sulfuric acid and the glass walls of retaining vessels. In particular, Foils A59-63 gave the same type of plot as Foil A58. One exception among foils anodized in chromic acid was the plot for Foils A44-47 which produced a curve which was slightly concave upward. Figure 32, the H and J plot (Harkins and Jura) for A52, shows the more typical behavior. Figures 33-36, inclusive, show the deviations from the H and J straight line.

50. To apply the Harkins and Jura equation (16.2), it was necessary to determine the value of k for ethylene by measuring the adsorption of ethylene on a surface of known area. For this purpose, a sample of porous glass of known area (11) was used. Straight lines were obtained in the Harkins and Jura plots of $\log P/P_0$ vs. $1/n^2$, as typified in figure 37. Values of A in equation (16.1) were 1.81×10^{-2} and 1.73×10^{-2} cc² for two runs. Using the mean of these values and the area reported from nitrogen adsorption (120 sq m per gm), k in equation (16.2) is 5.19×10^4 cm⁻¹ for ethylene at -183°C.

51. The roughness factors calculated by the three methods are compared in table VI. The agreement is of the order usually obtained by these methods employing nitrogen as the adsorbate on solids with large surface areas.

TABLE VI
ROUGHNESS FACTORS BY SEVERAL METHODS FOR ETHYLENE ADSORPTION

Surface	Apparent Area	Roughness Factor		
		Pt. B	BET	H and J
A1	90.	1.86	1.5	1.9
A2	95.5	1.1	1.2	1.1
A4	12.5	11.0	10.2	12.2
A5	17.44	7.9	7.4	9.8
A6	95.5	83.5	77.9	87.
A7	96.2	66.1	66.1	79.
A42	25.4	86.0	78.9	102.
A43	10.3	81.8	76.	92.
A44-47	14.2	82.7	74.7	85.
A48	11.0	35.7	40.	46.
A49	10.3	36.1	36.1	37.
A50	25.3	19.7	21.	23.
A52	11.4	77.4	74.4	91.
A55	10.8	245.	226.	----
A58	3.3	450.	406.	----
A59-63	5.68	619.	556.	----
A42 *	25.4	5.6	6.1	6.5
A44-47 *	14.2	29.2	40.9	36.
Glass †	----	113 §	129 §	----
Glass ‡	120.	5.3	5.4	----

* Sealed by exposure to water vapor at 100°C for 30 minutes.

† Porous Glass.

‡ Glass bulb fused and then cleaned successfully with chromic acid, ethyl alcohol and nitric acid.

§ Area in square meters per gram.

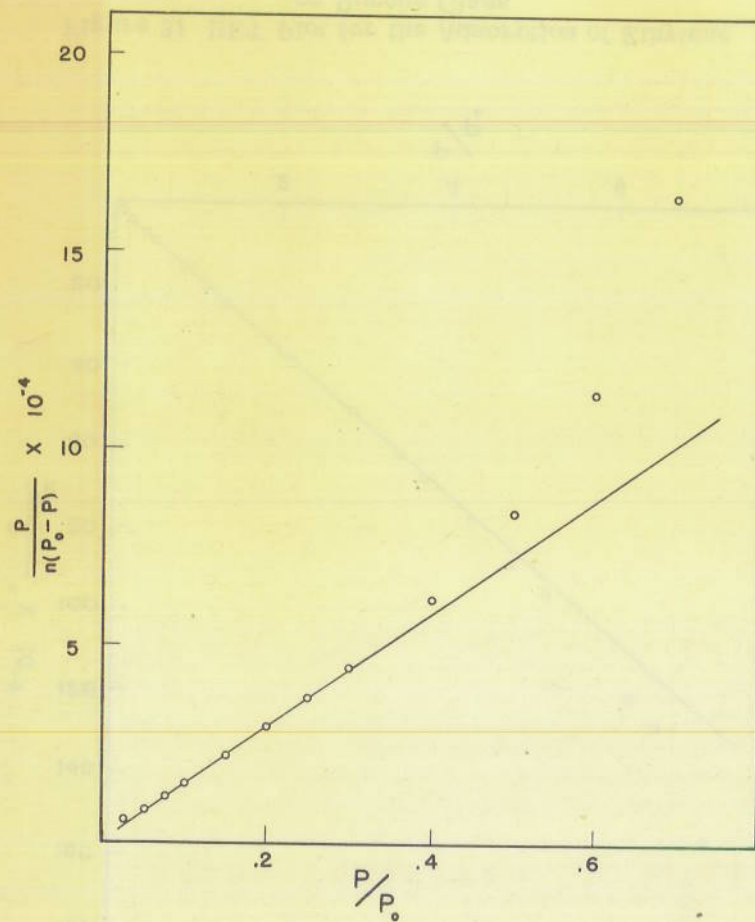


Figure 29 BET Plot for the Adsorption of Ethylene on Foil A6

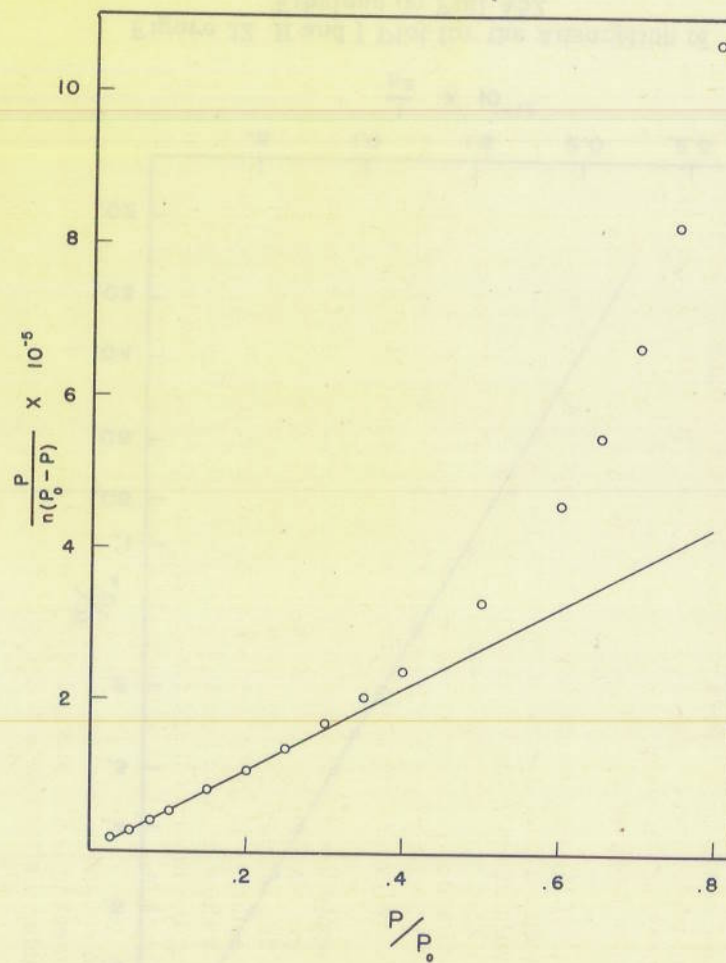


Figure 30 BET Plot for the Adsorption of Ethylene on Foil A42

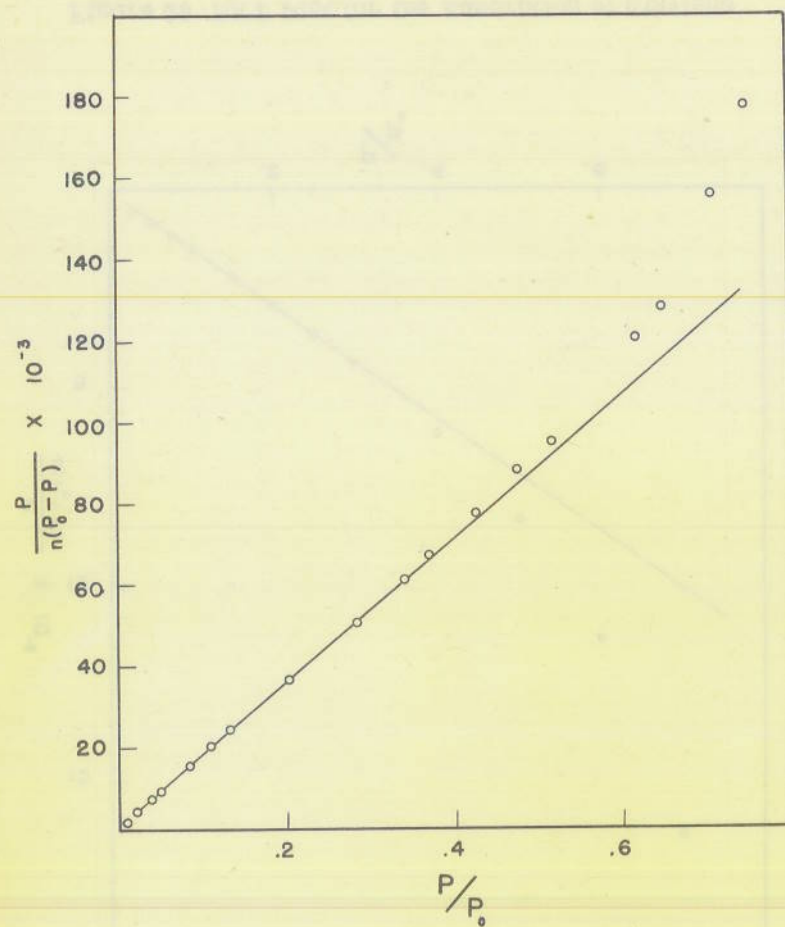


Figure 31 BET Plot for the Adsorption of Ethylene on Porous Glass

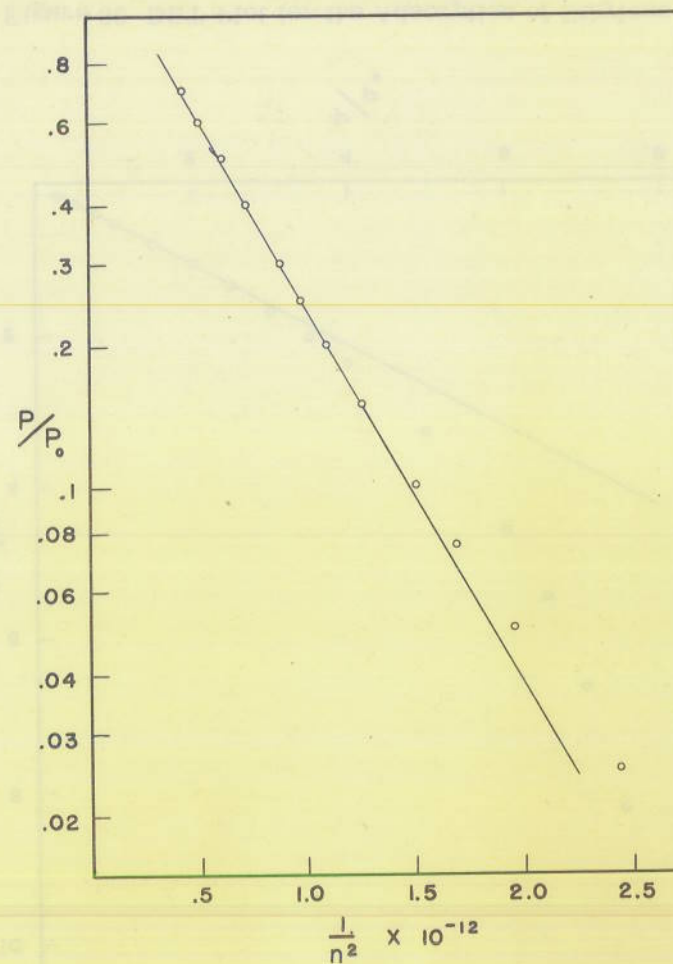


Figure 32 H and J Plot for the Adsorption of Ethylene on Foil A52

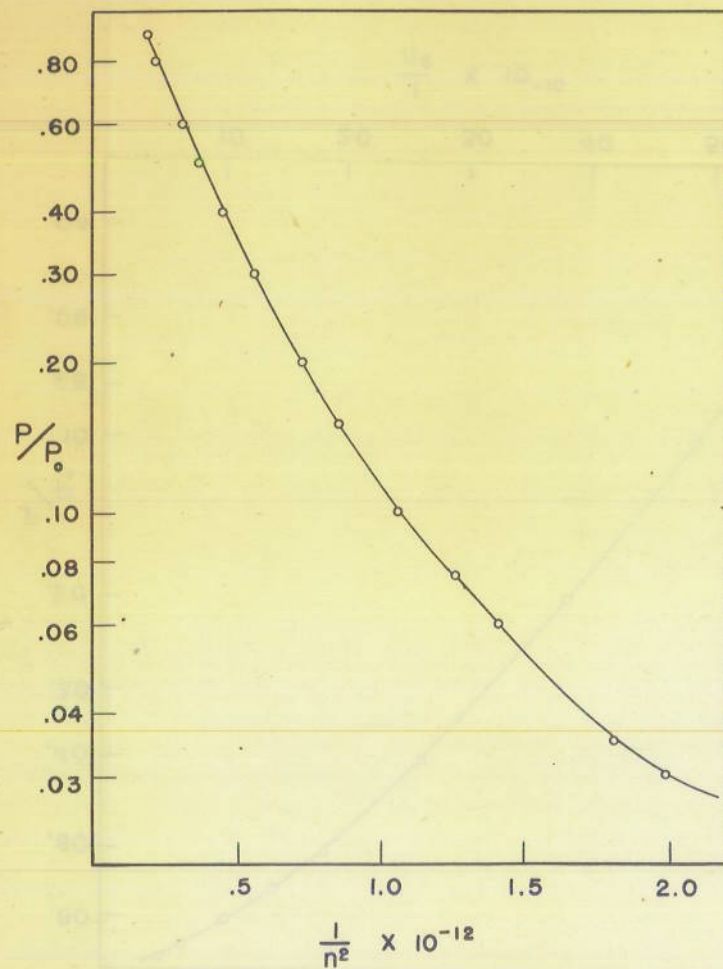


Figure 33 H and J Plot for the Adsorption of Ethylene on Foils A44-47

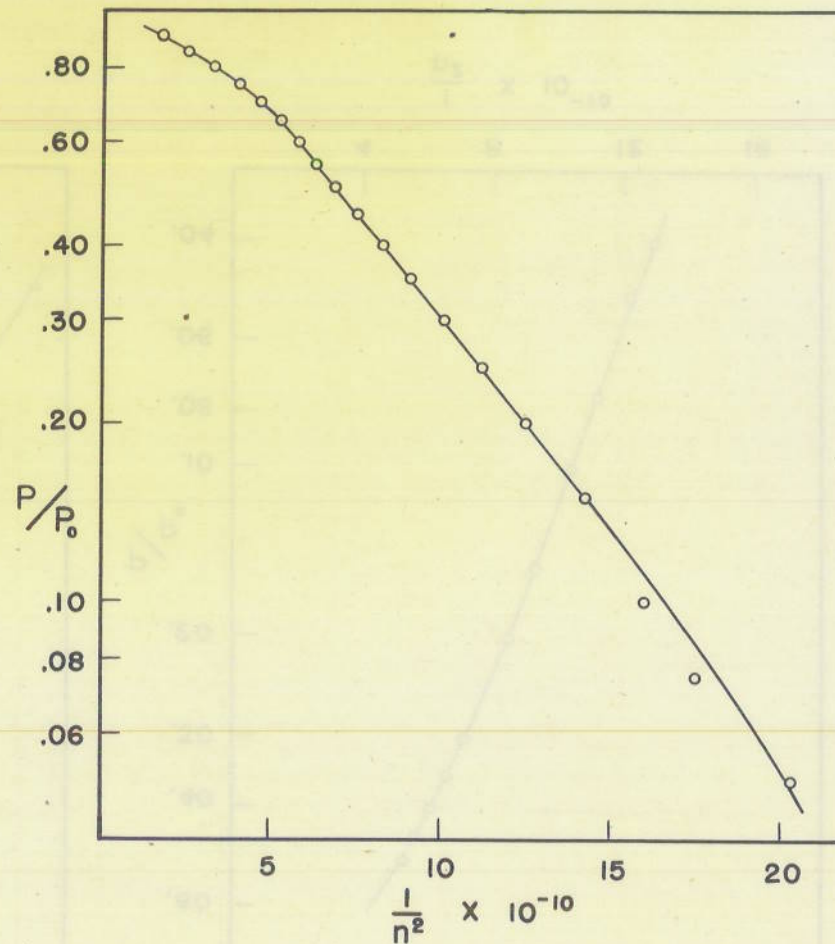


Figure 34 H and J Plot for the Adsorption of Ethylene on Foil A55

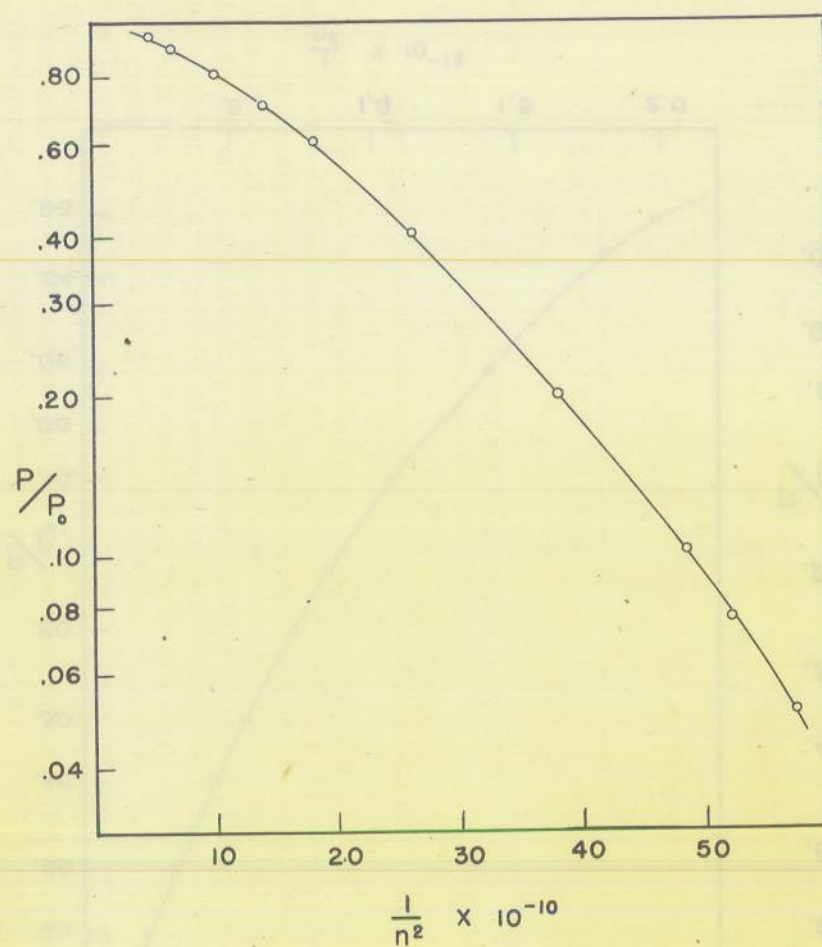


Figure 35 H and J Plot for the Adsorption of Ethylene on Foil A58

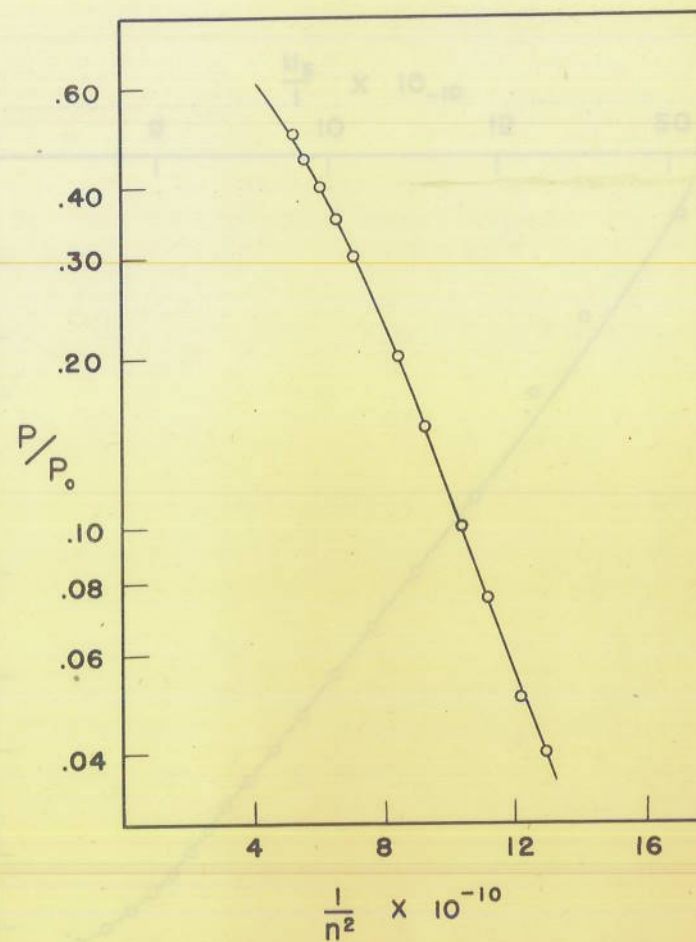


Figure 36 H and J Plot for the Adsorption of Ethylene on Foils A59-63

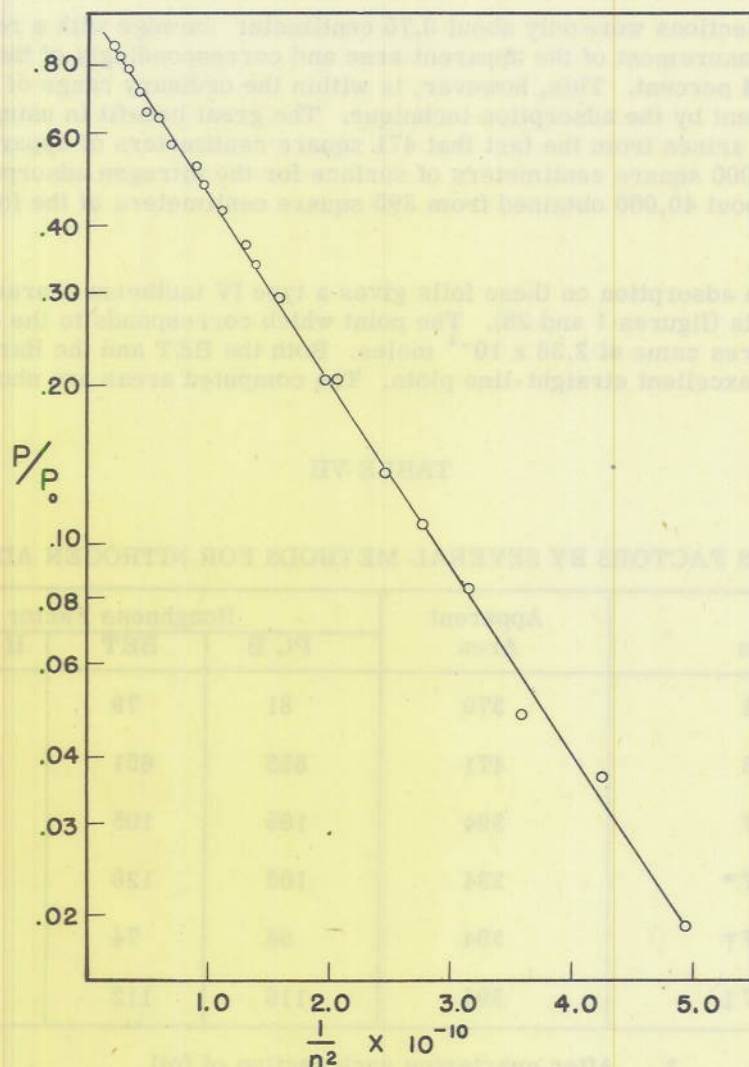


Figure 37 H and J Plot for the Adsorption of Ethylene on Porous Glass

Comparisons of Nitrogen and Ethylene Adsorptions on Anodized Aluminum

52. To compare nitrogen and ethylene adsorption on the same batch of anodic foil, three runs were made in which 4 or 5 sheets of 6 x 8 centimeter foil were anodized by the same procedure. A small section was taken for ethylene adsorption while the remainder was applied to nitrogen adsorption. A material having as high a roughness factor as possible is desirable for the nitrogen adsorption studies. On the other hand, a large roughness factor requires the use of a small piece of foil in ethylene adsorption with consequent increased uncertainty as to its area and to possible edge affects. The runs on Foils A59-63 were more suitable for intercomparison than the others. In this case, a section of foil was taken from the center of each of the five sheets. The total area used in the ethylene experiments, 5.68 square centimeters was far too large for convenience and required many fillings of the gas burette (the McLeod gage bulb) with, however, no consequent loss in accuracy of measurements of actual adsorption.

The individual sections were only about 0.75 centimeter on edge with a resulting possible error in the measurement of the apparent area and correspondingly of the roughness factor of about 4 percent. This, however, is within the ordinary range of accuracy of area measurement by the adsorption technique. The great benefit in using foil anodized in sulfuric acid arises from the fact that 471 square centimeters of apparent surface gave about 300,000 square centimeters of surface for the nitrogen adsorption runs in contrast with about 40,000 obtained from 390 square centimeters of the foils anodized in chromic acid.

53. Nitrogen adsorption on these foils gives a type IV isotherm characteristic of porous materials (figures 1 and 28). The point which corresponds to the complete filling of the pores came at 2.38×10^{-3} moles. Both the BET and the Harkins and Jura equations gave excellent straight-line plots. The computed areas are shown in table VII.

TABLE VII

ROUGHNESS FACTORS BY SEVERAL METHODS FOR NITROGEN ADSORPTION

Surface	Apparent Area	Roughness Factor		
		Pt. B	BET	H and J
A51-54	370	81	79	84
A59-63	471	653	651	607
A44-47	394	105	105	106
A44-47 *	394	105	128	103
A44-47 †	394	64	74	72
A44-47 ‡	394	116	112	130

* After quartering each section of foil (Paragraph 54).

† Sealed after second area determination, by exposure to water at 100°C for 30 minutes.

‡ Subjected to second sealing operation after third area determination.

54. Foils A44-47, cut into pieces about 1.2 x 3 centimeters, were used as adsorbents for nitrogen. To determine the magnitude of edge effects, these sheets were quartered after the first run to give pieces about 0.6 x 1.5 centimeters, sealed into a smaller sample tube and another adsorption run was made. The results, table VII, show a very slight effect.

55. Nitrogen adsorption on Foils A51-54 was run on 1.2 x 3 centimeter sections. The results are tabulated along with those for foils A44-47 and A59-63 in table VII. Ethylene adsorptions on foils of this group are reported in table VI.

Comparisons of Nitrogen and Ethylene Adsorptions on Porous Glass

56. Two successive ethylene runs were made on a sample of 5.75 milligrams of 120-200 mesh porous glass. The runs, agreeing within 2 percent, yielded type II or IV isotherms. Good straight lines were obtained in the Harkins and Jura plots, yielding values of 1.81×10^{-2} and 1.73×10^{-2} cc² for A in equation (16.1).

57. A nitrogen adsorption run was also made on a 0.281-gram sample of the porous glass in the Chemistry Laboratory of Northwestern University. Its data is not presented here, but, by the BET plot, the area was 120 square meters per gram in agreement with the results of Emmett and DeWitt (11) and of Beebe, Beckwith and Honig (4). For comparison with the results in table VI, the area of 5.75 milligrams of porous glass would be 6900 square centimeters as determined by nitrogen adsorption.

The Saturation Pressure of Ethylene at -183°C

58. Ethylene on Foils A59-63 gave a type of isotherm which could not be fully characterized since the pressure had been carried only to about 10 microns (figure 23). Furthermore, since a rather short straight-line region was obtained in the BET plot using the observed saturation pressure, the effect of other assignments of P_0 was investigated. An increase in the saturation pressure reduced the slope and increased the correspondence with a straight line predicted by the BET equation. The area calculated from these plots and the corresponding roughness factors are given in table VIII.

TABLE VIII

RESULTS OF BET PLOTS OF DATA FOR ETHYLENE ADSORPTION
ON FOILS A59-A63
(APPARENT AREA - 5.68 Sq. Cm.)

P_0 (microns)	n_{m_6} $\times 10^6$	Area sq. cm. $\times 10^{-3}$	Roughness Factor	Straight Line Region	
				P/P_0	P (microns)
21.6	2.98	3.16	556	.014 - .18	0.3 - 4
23.6	3.02	3.20	563	.013 - .165	.3 - 4
25.3	3.06	3.24	570	.012 - .19	.3 - 4.5
28.6	3.14	3.33	586	.018 - .24	.5 - 7
33	3.25	3.44	606	.03 - .3*	1.0 - 10*
38.5	3.50	3.71	653	.05 - .26*	2. - 10*
44	3.76	3.98	702	.11 - .22*	5 - 10*
Point B	3.32	3.52	619		

* The adsorption isotherm was not carried beyond 10 microns so that the upper limit to the straight line region was not ascertainable.

59. Because the value of P_0 was not very reproducible in different runs, this treatment was also tried with the data for Foils A6 and A43 and for porous glass. A considerable number of points were obtained on their isotherms. Foils A6 and A43 produced isotherms which were characteristic of the anomalous type. In general, increasing the value of P_0 increased the length of the straight-line region in the BET plot as it did for Foils A59-63. The results are presented in tables IX, X and XI. The roughness factors from the Harkins and Jura method and the "Point B" method are included for direct comparison.

TABLE IX
EFFECT OF ASSIGNMENT OF P_0 ON COMPUTED AREA OF FOIL A6

(95.5 Sq. Cm.)

Method	P_0 (microns)	n_m $\times 10$	Area (sq. cm.)	Roughness Factor	Straight Line Region	
					P/P_0	P (microns)
BET	18	6.53	7030	73.6	.023 - .28	.4 - 5
BET	20.3	7.01	7440	77.9	.04 - .29	.8 - 6
BET	25	7.84	8310	87.0	.07 - .26	1.7 - 6.5
BET	29	8.20	8690	91.0	.065 - .35	1.9 - 10
BET	33	8.79	9320	97.6	.06 - .36	2. - 11.5
BET	37	9.39	9950	104.1	.11 - .39	4. - 14
Pt. B.	----	7.6	----	84	----	----
H and J	----	----	8300	87.0	----	----

TABLE X
EFFECT OF ASSIGNMENT OF P_0 ON COMPUTED AREA OF FOIL A43

(10.2 Sq. Cm.)

Method	P_0 (microns)	n_m $\times 10$	Area (sq. cm.)	Roughness Factor	Straight Line Region	
					P/P_0	P (microns)
BET	18	6.98	740	72.5	.036 - .21	.6 - 4
BET	21.6	7.34	778	76.3	.03 - .21	.6 - 4.5
BET	25	7.56	801	78.5	.03 - .24	.75 - 6
BET	29	7.87	834	81.7	.035 - .28	1.0 - 8
BET	33	8.08	856	84.0	.03 - .33	1.0 - 11
BET	37	8.66	918	90.0	.05 - .32	1.9 - 12
Pt. B.	----	7.85	835	81.8	----	----
H and J*	----	----	927	90.8	----	.86 - 6
H and J*	----	----	955	93.6	----	3 - 11
H and J†	----	----	----	91.7	----	----

* It was possible to draw two straight lines of slightly different slope.

† Mean of two H and J values.

TABLE XI
EFFECT OF ASSIGNMENT OF P_0 ON COMPUTED AREA
OF POROUS GLASS (5.75 mg.)

Method	P_0	n_m $\times 10^6$	Area (sq. cm.)	Straight Line Region	
				P/P_0	P(microns)
BET	19.8	5.63	5960	.03 - .25	.6- 5
BET	21.6	5.78	6120	.04 - .31	.9- 7
BET	22.5	5.84	6190	.04 - .32	.9- 7
BET	23.6	5.99	6350	.04 - .32	1.0-7.5
BET	26	6.27	6650	.05 - .4	1.3-10
BET	29	6.60	6990	.065 - .3	1.7-8.7
Pt. B	----	6.13	6490	----	----

DISCUSSION

Adsorption Area of the Ethylene Molecule

60. Wooten and Brown (5) used 17.55×10^{-16} square centimeters as the surface area of an ethylene molecule, a value derived from X-ray analysis of the crystalline solid. It corresponds to 1.06×10^9 square centimeters per mole. The measurement of both nitrogen and ethylene adsorption on foils and on porous glass (tables VI and VII) permits a check on this value. Applying the observed value of P_0 to Foils A59-63 the area computed from ethylene adsorption by the BET method lies 15 percent below that derived from nitrogen adsorption by the BET or Point B methods for Foils A59-63. Taking a higher value of P for ethylene, using Point B for ethylene or using the Harkins and Jura method for nitrogen give closer agreement. From these data, one might conclude that the area per mole of ethylene ought to be increased 5-10 percent. From the results with porous glass a similar conclusion would be reached. The average area of the sample as determined by ethylene was about 6250 square centimeters. Nitrogen adsorption gave 6900 square centimeters. Throughout this report, however, areas have been computed for ethylene adsorption by the BET or Point B method using 1.06×10^9 square centimeters per mole of ethylene in accordance with the original procedure of Wooten and Brown. For the Harkins and Jura method with ethylene, 5.19×10^4 has been used as the value of the constant k in equation (16.2). This is derived from an average of the two values of A in paragraph 50 and an assumed area of 0.69 square meters for the sample of porous glass. Results with Foils A44-47 and A51-54 indicate similar discrepancies but are not to be considered as reliable as the two cases cited here.

Application of Equation Assuming a Limited Number of Molecular Layers

61. The isotherms, save those on porous glass and on aluminum anodized in sulfuric acid, exhibited a linear portion which extended to the saturation pressure (paragraph 47). Just before the saturation pressure, the quantity adsorbed was no more than twice to thrice that adsorbed at point B. It was, therefore, of interest to test equation (14.1) against the measured data. Using the experimental saturation pressure, values of $j = 3$ and $c = 100$ give in general about the best fit. The experimental data obey this equation up to distinctly higher pressures than the one for which j is unlimited. The region of deviation from the equation at low pressures is apt to be somewhat more extensive.

Several areas computed by this method may be cited for comparison with the results of Table XII. For Foil A1, $F = 1.56$; Foil A4, $F = 10.6$; Foil A43, $F = 76$ and for Foil A42 after sealing, $F = 5.9$. The method was not applied generally because there seemed to be no *a priori* reason for the number of layers being limited save by mechanical considerations such as pores or narrow but long crevices. Furthermore, precisely those surfaces, which are known to be porous and of the smallest pore diameter, exhibit the normal type isotherm, namely, porous glass and sulfuric acid anodic film. Also, they lead, within the experimental error, to the same value of the area as the use of the experimental value of the saturation pressure in the unlimited equation (13.1).

TABLE XII
SUMMARY OF ROUGHNESS FACTORS FROM ADSORPTION
OF ETHYLENE ON ALUMINUM FOILS

Surface	Apparent Area sq. cm.	BET $P_0 = 21^*$	Roughness Factor		
			BET $P_0 = 33$	Pt. B.	H and J
A1	90	1.5	1.8	1.9	1.9
A2	95.5	1.2	1.1	1.1	1.1
A4	12.5	10.2	12.8	11.0	12.2
A5	17.44	7.4	7.9	7.9	9.8
A6	95.5	77.9	97.6	84	87
A7	96.2	66.1	84	66	79
A42	25.4	78.9	89	86	102
A42†	25.4	6.1	7.0	5.6	6.4
A43	10.2	76	84	82	92
A44	14.2	74.7	84.7	77.7	85
A44†	14.2	40.9	----	37.5	36
A48	11.0	40	----	39.7	46
A49	10.3	36.1	----	36.2	37
A50	25.3	21	----	19.4	23
A52	11.4	74.4	----	79.4	91
A55	10.8	226	265	246	----
A58	3.30	406	490	450	----
A59-63	5.68	556	606	619	----

* Approximate value; calculated with observed saturation pressures in Table III.

† Sealed by exposure to water vapor at 100°C for 30 minutes.

The Proper Assignment of P_0

62. A more likely explanation of anomalous isotherms is that P_0 is properly the vapor pressure of liquid ethylene, not solid ethylene. Thus, the isotherms are abruptly terminated at $P_0 = 0.5$ or so by condensation of solid ethylene. Egan and Kemp (17) reported the heat of fusion of ethylene to be 800 calories/mole at its melting point, 103.95°K.

By the Clausius-Clapeyron equation:

$$\frac{d \ln P(21)}{dT} = \frac{\Delta H(21)}{RT^2} \quad (62.1)$$

$$\frac{d \ln P(31)}{dT} = \frac{\Delta H(31)}{RT^2} \quad (62.2)$$

Here, 1 refers to gas, 2 to liquid and 3 to solid. The first equation is for the vapor pressure of the liquid, the second for the sublimation pressure of the solid. It follows that,

$$\ln \frac{P(31)}{P(21)} = - \frac{\Delta H(32)}{RT} + A \quad (62.3)$$

Since, at the melting point $P(31) = P(21)$,

$$0 = - \frac{800}{1.987 \times 103.95} + A$$

On solving,

$$A = 3.87 \quad (62.4)$$

Thus,

$$\ln \frac{P(31)}{P(21)} = - \frac{800}{1.987T} + 3.87 \quad (62.5)$$

At 90°K, the boiling point of oxygen,

$$\frac{P(31)}{P(21)} = 0.55 \quad (62.6)$$

That is, at 90°K, the ratio of the sublimation pressure to the vapor pressure should be about 0.55. It is assumed that $\Delta H(32)$ is independent of pressure. Thus, if the sublimation pressure of ethylene at 90°K is 21.6 microns, the vapor pressure of the liquid would be about 39 microns.

63. Referring to the results of the application of several values of P_0 to data on two foils which were typical of the anomalous isotherm type, Foil A6 and Foil A43 in tables IX and X, it is seen that increase in P_0 above the sublimation pressure of the solid continuously extends the region in which a straight line is obtained. On the other hand, the start of the straight line region occurs only at higher pressures. Beyond $P_0 = 33$ microns, this effect is augmented. The computed areas continuously

increase though not very rapidly. This effect is in agreement with the observation of Anderson (10) as described in paragraph 14. It does not seem possible by mere inspection of a series of BET plots based upon different values of P_0 to pick the proper value of P_0 . If Anderson's views are valid, the saturation pressure is not the best value to use in any case. All in all, a value of $P_0 = 33$ seems to give about the best results considering both the high and low pressure regions. A change of 20 percent in its value would lead to changes in area within the general uncertainty of the procedure. An inspection of table XII discloses that use of $P_0 = 33$ results in areas 12-15 percent higher than those obtained with $P_0 = 21$. The value obtained by Point B is usually in somewhat better agreement with the $P_0 = 33$ value. This is also true of the area computed by the Harkins and Jura method. Accordingly, the area and roughness factor for each surface were determined by using the value of 33 microns as the saturation pressure in the BET plots. The values are compared with the others in table XII.

64. Beebe's (4) isotherms of krypton adsorption at -196°C apparently are of the same type as those of ethylene at -183°C , though Beebe does not give his isotherms beyond $P/P_0 = 0.5$. He used the extrapolated vapor pressure of liquid krypton for P_0 . He points out that isotherms of carbon dioxide published by Brunauer and Emmett may be of this type. He also states that this is true for the adsorption of ethylene at -196°C in the work of Wooten and Brown (5). No isotherm at -196°C is of this nature, but mixed barium strontium carbonates produce such an isotherm at -183°C .

65. As exhibited in tables VIII and XI, the use of larger values of P_0 than the sublimation pressure also extends the straight line region of the BET plot for adsorbents which give normal isotherms, porous glass and Foils A59-63. The straight-line region, however, starts only at higher pressures. Computed areas rise with P_0 . The only apparent difference between the two classes of isotherms is that for the normal type, for $P_0 = 33$ microns, points fall below the extrapolated straight line at higher values of pressure while for the anomalous type they rise above it.

66. A question of considerable interest is posed by the discovery of the two kinds of isotherms with different saturation pressures. It will be possible to interpret such an occurrence only on the basis of some theory of multilayer adsorption. For P_0 to be the saturation pressure either of the liquid or of the solid, the heat of evaporation from the 2nd, 3rd and----- n-th layers must be the same as the heat of evaporation or sublimation respectively of the bulk material. In layers but two or three molecules deep and at temperatures near the melting point of the solidified gas, it is not implausible that the nature of the adsorbent, its intermolecular distances, chemical composition, etc., should influence the nature of the condensed layer. That is, in layers but a few molecules deep, there is no reason that the melting point of the adsorbed layer should be that of the bulk solidified vapor. Thus, in cooling an adsorption system, there is no reason to expect a change in isotherm type at the bulk melting point of the vapor. Just below the melting point, the isotherm might approach the experimental $P = P_0$ line (sublimation pressure) with a finite slope and at still lower temperatures the straight line would reach the $P = P_0$ line. At sufficiently low temperatures, an S-shaped isotherm which approaches the $P = P_0$ line with infinite slope will again be found. At intermediate temperatures, the type of isotherm may depend upon the nature of the surface of the adsorbent. It may be noted that at the point at which the isotherms on porous glass and sulfuric acid anodic film begin to rise above the straight line, just about one and one-half layers have been adsorbed.

67. At an intermediate temperature, the porosity of the adsorbent may favor the S-shaped isotherm (really Type IV, figure 1) if the pores are sufficiently fine so that 1 or 2 adsorbed layers will result in molecules adsorbed on opposite sides of a pore beginning to affect one another. Owing to the steep rise of the isotherm beyond 9 microns, the adsorption isotherm of ethylene on porous glass may be of this type for the pores have an average diameter of but 25-30 Angstrom units. It may be recalled that the isotherms of the adsorption of ethylene on the pyrex glass walls of the sample container was of the abnormal type. It is true that the next most porous material studied was the sulfuric acid anodized film which is reported to have a pore diameter of about 100 Angstrom units (14, 18). It is however, difficult to see how an adsorbed film two layers thick could be of much consequence in this case.

Roughness Factors

68. A summary of area determinations is given in table XII. Areas have not been computed by the use of $P_0 = 33$ for Foils A48, A49, A50 and A52. These foils are films formed in chromic acid and their behavior should resemble that of Foils A42, A43 and A44.

69. The original aluminum foil seems to be comparatively rather smooth. Figure 38 shows an electron micrograph of a replica of the surface, the contrast of which had been increased by the gold-shadowing technique of Williams and Wychoff (15). Optical photomicrographs, taken at 500X, disclosed no interpretable surface structure save fine rolling lines which actually are visible to the eye by diffraction effects. As to how much this results from surface irregularity and how much from the orientation of constituents during rolling is problematic. For Foil A3, with a history similar to that of Foils A1 and A2, a roughness factor of about 1 was found. These foils were all measured as a square section of foil rolled into a rather open spiral for subsequent dip treatments. As a result, the bulb volume and area were rather large compared with the foil area. The roughness factor for the original foil was probably somewhere in the vicinity of 1.5.

70. Treatment of aluminum foil with 5 percent Na_2CO_3 at 86°C results in considerable increase in area, the roughness factor measuring about 10 (Foils A4 and A5). An electron micrograph of a replica showed pits ranging in diameter from a few microns down. Some of the larger pits seemed to be visible in an optical photomicrograph. At least in dark field illumination the treated foil had many more light scattering centers than the untreated. After treatment the foil was uniformly wet with water which was not true of the foil which had been merely solvent cleaned. The treated foil had a surface texture which was slightly different to the naked eye than that of the untreated.

71. Treatment with the chromic acid-sulfuric acid mixture resulted in a very large increase in area to a roughness factor of about 80-90 (Foils 6 and 7). The foil after treatment was uniformly wettable with water and had a satin-appearance. Optical photomicrographs disclosed nothing. Figure 39 is an electron micrograph of a replica the contrast of which has been increased by gold-shadowing (15). The very rough surface produced by this treatment is shown. The structure is, however, all below the resolution of an optical microscope.

72. Foils A42, and A43, Foils A48 and A49, and Foil A50 form a series of aluminum foils anodized in chromic acid for 42, 22 and 11 minutes, respectively. Agreement within the two pairs is excellent. The roughness factors are about 86, 36 and 20, and are approximately proportional to the time of anodization as illustrated in Figure 40. Since the roughness factor of the original aluminum surface is small, the adsorbing surface



Figure 38 Electron Micrograph of Untreated Aluminum Foil, 8000 X



Figure 39 Electron Micrograph of Aluminum Foil Treated
with Mixed Chromic-Sulfuric Acids

must lie in the capillary structure of the anodic film and should be proportional to the length of the capillaries, that is, proportional to the thickness of the film and thus to the time of anodization.

73. Foils A44 and A52 were prepared exactly as Foils A42 and A43, save that the foil was treated in the chromic acid-sulfuric acid solution before anodizing. The roughness factors are, however, substantially the same. It might have been expected that a larger relative area would have been found, owing to the greater roughness of the original aluminum. Whether the anodizing process results in an electropolishing effect is difficult to say. The effect of pretreatment on the surface area of the final anodized film can be elucidated only by further study.

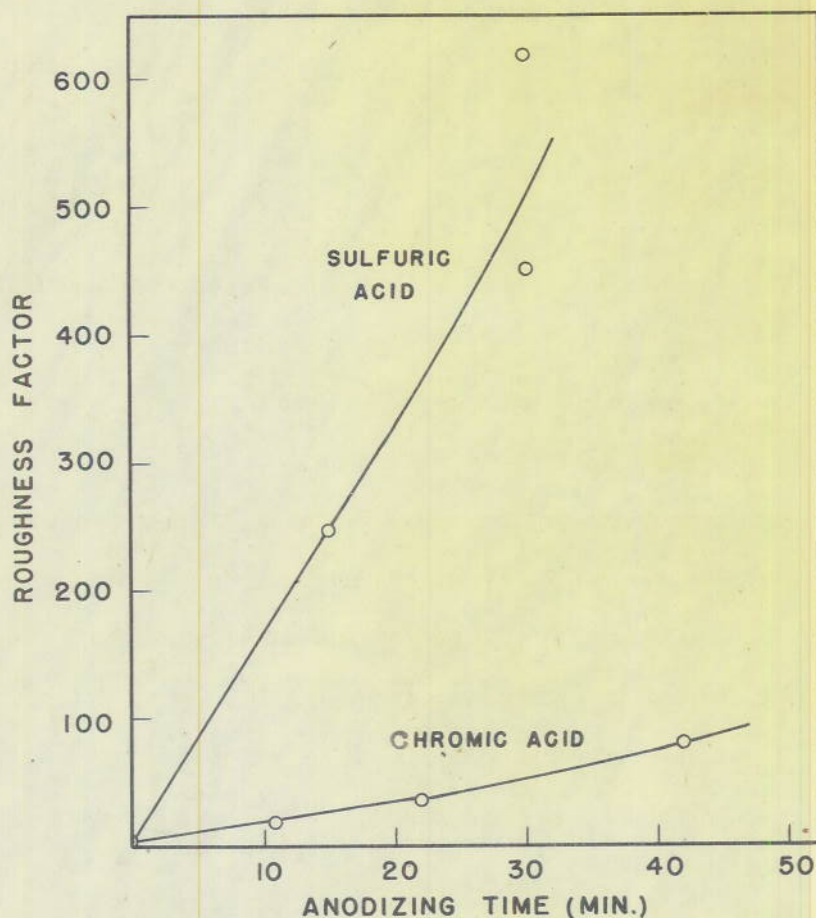


Figure 40 Effect of Anodizing Time on Roughness of Aluminum Foil

74. Foils A42, A43, and A44 were sealed by treating with steam for 15 minutes. This process converts the surface and presumably the walls of the capillaries to boehmite, α - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The greater volume of the resulting boehmite is believed to result in sealing of the pores (13). The data on Foils A42 and A44 are consistent with this. The roughness factor for Foil A42 is less than 10 percent of that before sealing. Foil A49 was sealed and the resulting roughness factor was less than 10, but, as with Foil A43,

the very small adsorption did not permit its accurate determination. The roughness factor of Foils A44-47 was decreased but 60 percent by sealing. The explanation of this is not clear, but incomplete sealing is indicated. Increase in roughness during prolonged exposure to hot water suggests conversion to more voluminous aluminum hydroxide.

75. The sulfuric acid anodized foils are very rough, for equal thickness of film about three times as rough as the chromic acid foils and for equal anodizing times about eight times as rough. Foils A55 and A58 were merely solvent cleaned before anodizing. The roughness factors are proportional to the anodizing times (figure 40). Foils A59-63 were treated with the chromic-sulfuric acid mixture before anodizing. In contrast to the case of the chromic acid-anodized foils an increased area is found. The greater roughness factors of the sulfuric acid foils is in agreement with the electron microscopic observation (14) of the smaller pore diameter and greater pore density.

76. As determined by nitrogen adsorption, the roughness factor of Foils A59-63 is 652. The volume of nitrogen in the pores, per square centimeter of foil, is

$$\frac{2.38 \times 10^{-3} \times 28}{0.808 \times 471} = 1.75 \times 10^{-4} \text{cc} \quad (76.1)$$

2.38×10^{-3} = moles of nitrogen corresponding to complete pore filling.

471 = square centimeters of anodized foil.

0.808 = density of liquid nitrogen at -195.8°C .

28 = molecular weight of nitrogen.

The measured area and volume per square centimeter of foil is as follows:

$$\text{area} = 2\pi nrL = 652 \text{ square centimeters} \quad (76.2)$$

$$\text{volume} = \pi r^2 nL = 1.75 \times 10^{-4} \text{ cubic centimeters} \quad (76.3)$$

where:

r = radius of the capillaries

n = number of capillaries per square centimeter

L = thickness of the anodic film, 1.25×10^{-3} centimeters

Solving the above equations,

$$r = 5.35 \times 10^{-7} \text{ centimeters} = 107 \text{ Angstrom units}$$

$$n = 1.55 \times 10^{11}$$

The average pore diameter, 107 Angstrom units, is in reasonable agreement with the results of Fischer and Kurz (18) and Edwards and Keller (14) who prepared very thin anodic layers on electropolished aluminum and examined these in the electron microscope. The electron micrographs of Fischer and Kurz give about 150 Angstrom units as the pore diameter and about 0.8×10^{11} as the number of pores per square centimeter. Edwards and Keller report 100 and 2.7×10^{11} respectively.

CONCLUSIONS AND RECOMMENDATIONS

77. Ethylene adsorption isotherms at 90°K permit the determination of surface areas probably to within 20 percent of the true value. The relative accuracy is probably about 10 percent.

78. The method is suitable for the determination of true surface areas of metal foils. Foils are not convenient adsorbents because the necessity of avoiding edge effects with smooth foils precludes cutting the foil into small pieces for efficient packing. Thus, the sample bulb is much larger than it would be for a powder of similar area. The corrections for the volume and area of the bulb become large compared with the adsorption on the adsorbent. For smooth foils, at least 200 square centimeters of foil ought to be used and ingenuity should be exercised to keep the sample bulb as small as possible. With foils having a roughness factor which exceeds 5, no trouble arises.

79. Most of the adsorbents which have been studied in this investigation give an unusual type of isotherm with ethylene at -183°C. The straight line portion of the adsorption isotherm extends to the saturation pressure. Apparently the determining saturation pressure for the isotherm is not that of the solid ethylene but that of the liquid. At -183°C, the latter is nearly twice the former. Thus, at a true relative pressure of 0.5, the adsorption isotherm is interrupted by the formation of solid ethylene. The uncertainties involved in this situation affect the surface areas only to within the general uncertainty and, while of considerable theoretical interest, do not prevent accurate surface area measurements.

80. In general, the Brunauer, Emmett and Teller equation applies to the adsorption of ethylene with a saturation pressure of 0.021 millimeters about as well as to that of nitrogen at 760 millimeters.

81. The Harkins and Jura equation reproduces the data reasonably well save for sulfuric acid anodic films. Here it fails. The Harkins and Jura constant, k , is $4.19 \times 10^4 \text{ cm}^{-1}$ for ethylene on amorphous aluminum oxide at -183°C.

82. The surface areas computed for anodized aluminum disclose an extremely rough surface which substantiates the hypothesis of a porous structure for these films. Such very large roughness factors will go far in explaining the excellent adhesion of paint to anodized aluminum. Roughness of aluminum anodized in either sulfuric or chromic acid increases linearly with duration of the anodic treatment during the first half hour. After this, there are slight indications that the rate of roughening increases.

83. The sulfuric acid anodizing process produces films with a roughness factor about three times that of chromic acid anodized films of the same thickness. This is consistent with a greater pore number and lesser pore diameter. This does not necessarily mean that adhesion of paint to sulfuric acid film is greater. Consider, for example two anodic films, one of which has four times as many pores of half the diameter of the other. Then if failure of the paint-surface bond results from fracture of the paint cylinders which fill the pores, equal strengths of adhesion will result since an equal cross section of material is broken. But the film of the greater pore number has twice the roughness factor.

84. "Sealing" anodized aluminum appears to reduce considerably the number and internal area of the pores. This will, no doubt, hinder the access of corrosive materials

to the aluminum surface, but it must be considered that the decrease in roughness may reduce the paint adhesion.

85. The technique described in this report is to be applied to practical alloys of aluminum in the sheet form. The studies will establish the relation of surface roughness and porosity to the conditions of anodization.

86. Upon completion of the investigation of paragraph 85, the results should be correlated with chemical forces of adhesion which are involved in equation (5.1). The procedures for determining these will be outlined in a subsequent report.

87. The technique of measuring surface areas is sufficiently reliable to be applied to steel surfaces. It is very desirable to add these to the program.

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