Adsorption on Active Magnesia 1. Surface Areas, Pore Structures, and the Nature of the Adsorption of Nitrogen, Argon, and Iodine.

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ADSORPTION ON ACTIVE MAGNESIA

1. Surface Areas, Pore Structures, and the Nature of the Adsorption of Nitrogen, Argon, and Iodine.

* * *

by

William Comstock Walker

* * *

A DISSERTATION

Presented to the Graduate Faculty

of Lehigh University

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April 1, 1946 — Date

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Accepted, 15 April, 1946
Date

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INTRODUCTION

Recent investigations have shown that active magnesium oxide has a place of its own in the fields of adsorption and catalysis. It is unique in being the only commercial product possessing high surface area and mechanical strength combined with a high degree of basicity and an ionic crystal lattice. These attributes give it unusual adsorptive and catalytic properties only a few of which have been investigated.

The commercial active magnesias have been found to be excellent adsorbents for the removal of fluoride from drinking water (1), silica from boiler water (2), fatty acids from petroleum ether (3), and impurities from petroleum lubricants, dry-cleaning solvents, and other nonaqueous and unreactive fluids (4). They have proved useful also in the chromatographic separation of the carotenes (5).

Catalytically, active magnesia has been used extensively in the manufacture of synthetic rubber (6) and studied thoroughly in the dehydration of ethyl alcohol (7,8).

Most of the active commercial grades have been prepared by the light-burning of magnesium hydroxide obtained from sea-water bitterns. Activity is measured industrially by the adsorption of iodine from solution. The work reported here on the low-temperature nitrogen adsorption isotherms was initiated to correlate iodine adsorption with the specific surface areas and to obtain information about pore structures of these grades. After the unusual shape of the isotherms was discovered, the isosteric heat of adsorption of nitrogen on an active grade was determined. A model of the pore structure of active magnesia consisting of plates of a checkerwork of cubic holes and crystallites was found to explain the isotherm shapes and conform with independent observations.

Non-conformity of the data to the usual equations for determination of surface area, and lack of agreement between areas determined with different adsorbates, led to the presentation of a new theory for the mechanism of adsorption on active magnesia. In contrast to the widely accepted concept of close-packing of the molecules in the first unimolecular adsorbed layer, the new theory specifies that positions of maximum stability for adsorbed molecules exist at regular intervals on the solid surface. The formation of the first layer consists in the filling of these positions, and the area occupied by an adsorbed molecule is determined by closest arrangement of the molecules over these positions.

By use of this theory it was possible to show that adsorption of nitrogen and argon from the vapor phase and of iodine from solution all give the same area for active magnesia.

ADSORPTION MEASUREMENTS

The apparatus and procedure were essentially the same as described by Emmett and Brunauer (9,10) and others (11). (See Appendix A). Nitrogen was adsorbed at liquid nitrogen temperatures in a constant volume apparatus. Known volumes of nitrogen were added and the resulting pressures noted. The nitrogen added was either adsorbed on the chilled sample (0.1 to 0.3 g.) or occupied the dead space above it. The dead space volumes were measured at liquid nitrogen temperatures with helium. Since the accuracy of the adsorption measurements depends on the precision with which the dead space is kept constant throughout the experiment, the end of the dead space at the pressure manometer was equipped with a tungsten contact. When the mercury was raised to the proper level in the dead space arm of the manometer, a circuit was completed so that, through a relay, a one-watt neon bulb flashed on. Corrections to the dead space volumes for the deviation of nitrogen from the ideal gas laws were determined experimentally. These corrections varied considerably over the temperature range of the experiments.

The temperature of the bath surrounding the sample tube was measured with a nitrogen vapor pressure thermometer. The vapor pressure-temperature relationships were taken from the measurements of Giauque and Clayton (12). For the later experiments on the heat of adsorption over the temperature range 72 to 80°K., the temperature was controlled to 0.02°K. by pumping on the liquid nitrogen or liquid air bath in the manner described by Orr (13). The pump on the low temperature bath was actuated by means of a make-and-break contact in the nitrogen vapor pressure manometer and a relay.

Optimum degassing conditions were ascertained by studies made on the most active sample. Active magnesia sinters readily so that mild conditions must be utilized. A temperature of 250°C. and a pressure of 10^{-6}mm. Hg for one hour were chosen as standard conditions; for these conditions the losses of weight on degassing varied between 0.4 and 2.5%. Four hours degassing under these conditions led to a decrease in surface area of 1.6% below the one hour value and a decrease of 3.2% after twenty hours. The effects of degassing temperature on the area of the sample are shown in Figure 1. At 300°C. for one hour a sharp increase in surface area with a relatively large decrease in weight of the sample due to further decomposition of the residual hydroxide set in; at 350°C. for one hour this increase reached a maximum of 15%. At 400°C. and beyond, the measured area decreased from the maximum. Degassing at room temperature for one hour gave a surface area 7% below the one hour, 250°C. value.

(The useful temperature range for the commercial active magnesias is considered to extend to 400°C.)

A micro-gas analysis* was performed on the gases removed from Cl-Free Magnesia under the standard degassing conditions. Before subjecting the sample to the oven temperature (250°C.), it was evacuated for ten minutes at 22°C.

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* The author is greatly indebted to Messrs. Serfass and Muraca for carrying out this analysis.

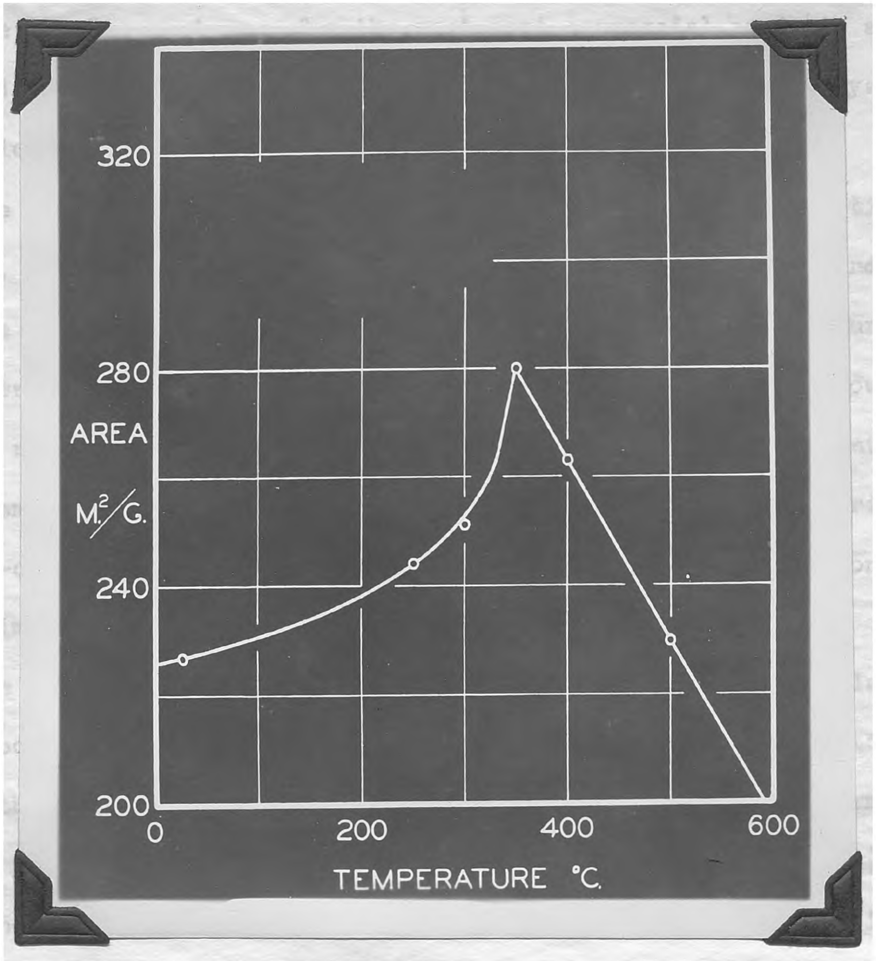

Figure 1.

Effect of Degassing for One Hour at Various Temperatures.

This gas was entirely carbon dioxide and water so that it may be concluded that these compounds rather than adsorbed air contaminate the surface of active magnesia.

ADSORPTION ISOTHERMS

The samples used were for the most part commercial products and were supplied by Westvaco Chlorine Products Corporation. Their analyses and preparation conditions are described in Appendix B.

The nitrogen adsorption isotherms at -195.8°C. for three active grades, 2642, 2652-S, and 2652, are given in Figure 2; and for 2642 and Chloride Free in Figure 3. Careful study was made of the high pressure points. For the powdered grade equilibrium was usually attained in one-half hour, but the pressure readings were taken after one hour. The nitrogen was introduced slowly and removed slowly (coming down the hysteresis loop) over a period of at least one-quarter of an hour. For the granular grades somewhat longer periods of time were required for equilibrium readings.

The isotherms in Figures 2 and 3 distinctly show a second plateau in the neighborhood of 0.8 relative pressure. The isotherms appear to be mixtures of the sigmoid Type II and the much more rare Type IV isotherms according to the widely-used classification of Emmett and Brunauer (14). Type IV isotherms possess second plateaus generally attributed to the filling of pores of uniform radius. From the shape of the isotherms, then, one would suspect rather uniform small pores with larger funnel-shaped openings coupled to the small pores or contributing separately to the total volume adsorbed at the saturation pressure.

The adsorption isotherms possess rather small hysteresis loops, as shown in Figures 2 and 3. Hysteresis is usually attributed to a narrowing of the pores at the openings (bottleneck picture) (15,16), or to the presence of pores with two open ends (17).

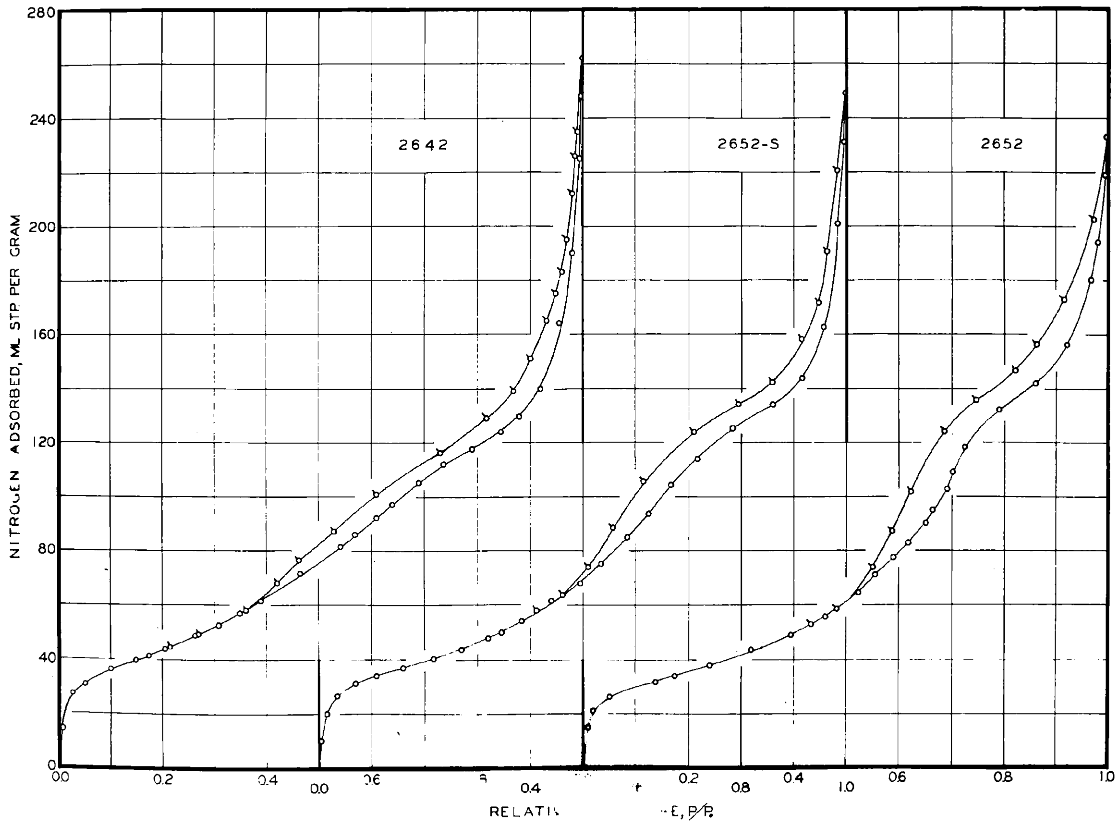

Figure 2.

Isotherms of Nitrogen Adsorption on Active Magnesias at -195°C.

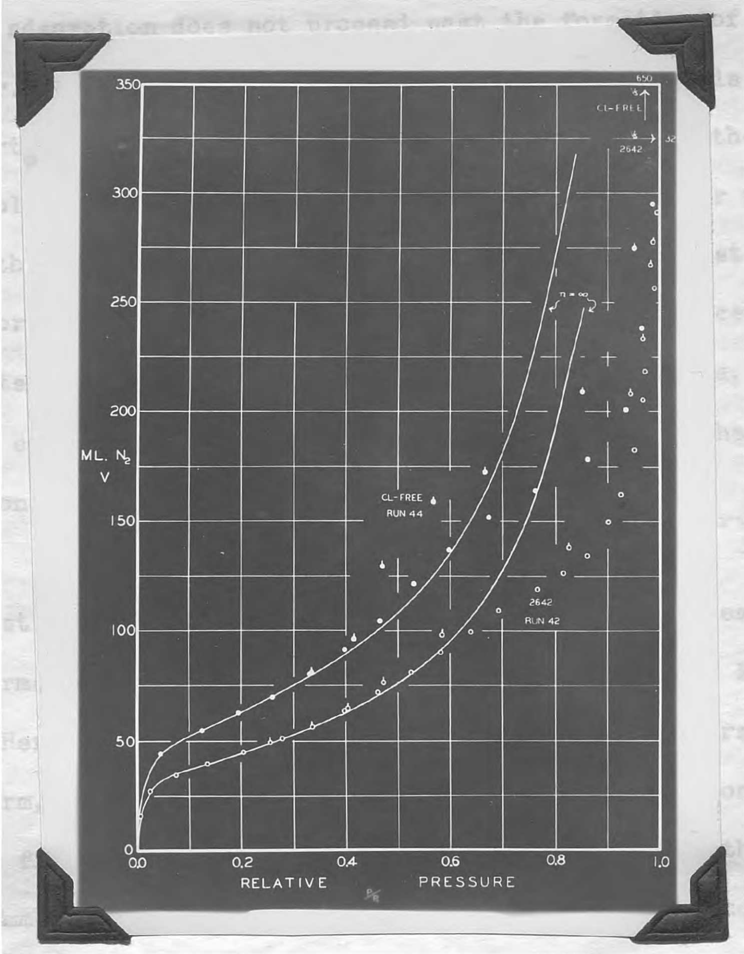

Figure 3.

Isotherms for Nitrogen Adsorption on Cl-Free Magnesia and Magnesia 2642.

In commercial practice activity is tested by the adsorption of iodine from carbon tetrachloride solution and reported as an empirical Iodine Number. (4) (See Appendix C). The isotherms of this adsorption are of the Langmuir type (Type I) in which adsorption does not proceed past the formation of the first unimolecular layer. The point determined for the Iodine Number is always on the horizontal portion of the isotherm and is thus indicative of the amount of iodine in the monolayer. This test has been extensively used for rapid determination of the activity of magnesia. In some cases the test appears to be deficient. For example, it has been found that in the presence of appreciable amounts of impurities such as silica, alumina, berylia, magnesium acetate, or other compounds, Iodine Number gives lower activity than does nitrogen adsorption.

CONVENTIONAL AREA DETERMINATIONS

The first and simplest method of determining surface areas from adsorption isotherms of Types II and IV was the B Point method of Emmett and Brunauer (10). Here they made use of the early idea that the first leveling off of the isotherm, at a relative pressure of about 0.1, corresponds to the completion of the first unimolecular layer of adsorbate covering the surface of the solid. Emmett and Brunauer found that this general idea could be made more precise by using the bottom of the central linear portion of the S-shaped isotherms (B Point) as the completion of the first unimolecular layer. Knowing the quantity of adsorbate required to complete this first layer, they could assign an area to each adsorbed molecule and thus calculate the total surface area of the solid adsorbent. These area assignments were made on the assumption that the molecules in the first adsorbed layer are packed in the same manner as in the liquid or solid state.

Later Brunauer, Emmett, and Teller (18) derived an equation on the basis of the kinetics of adsorption in more than one layer and with the assumption that the heat of adsorption is large in the first layer but equal to the heat of liquefaction in all succeeding layers. This equation was used very successfully in the calculation of the amount of adsorbate required to complete the first complete layer.

More recently Harkins and Jura (19) have derived an equation for calculating the surface area of the solid directly from the adsorption measurements without the necessity of assigning an area to a molecule of the adsorbate. This method is based on thermodynamics and may be used to determine the area of an adsorbed molecule.

The first of these methods to be applied to the adsorption of nitrogen on active magnesia was the BET method. According to this theory the volume of nitrogen required to complete a unimolecular layer, v_m, can usually be obtained from the slope and intercept of the linear $p/v(p_o-p)$ versus p/p_o plot (14,20).

$$\frac{p}{v(p_o-p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \, p/p_o \qquad (1)$$

In this equation p is the measured pressure; p_o is the condensation pressure of the adsorbate; v is the measured volume of gas adsorbed; and c is a constant related to the heat of adsorption. Equation 1 is a special form to which the more general equation 2 reduces when n is equal to infinity, n being the maximum number of molecular layers which can be adsorbed without encountering another solid surface and x the relative pressure (p/p_o).

$$V = \frac{v_m c x}{1-x} \; \frac{1-(n+1)x^n + nx^{n+1}}{1+(c-1)x - cx^{n+1}} \qquad (2)$$

The BET plots for Cl-Free Magnesia and for Magnesia 2642 are presented in Figure 4; they are typical of those for the other magnesias. In the 0.05 to 0.35 relative pressure region recommended for area determinations, the curves for all the samples are slightly but definitely concave to the relative pressure axis rather than linear.

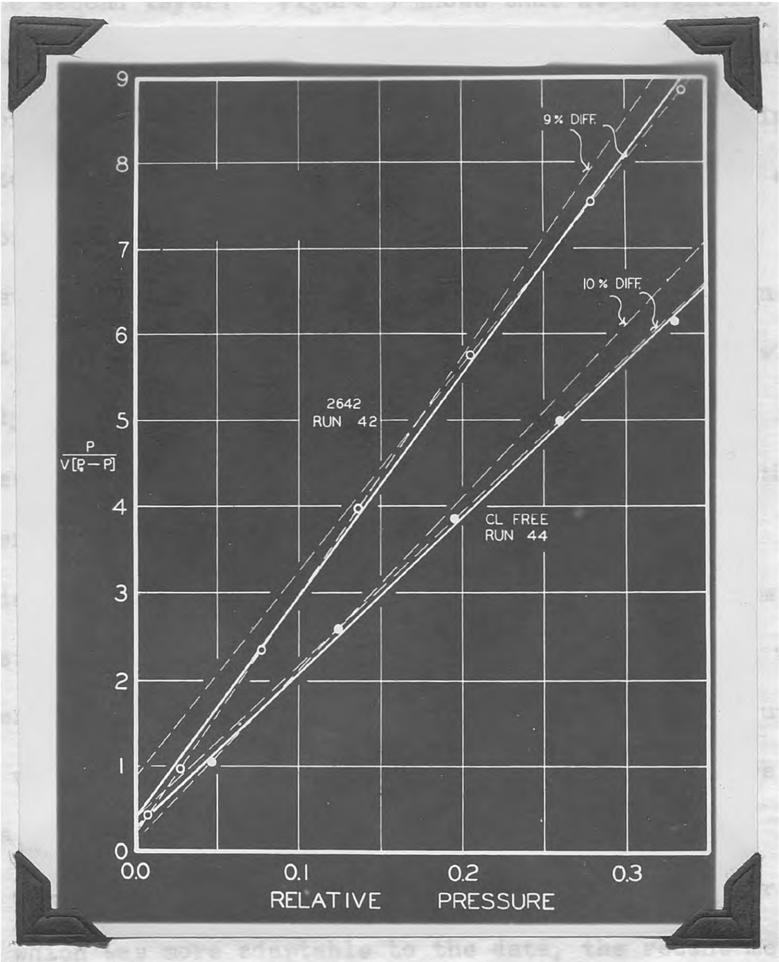

Figure 4.

BET Plots for Cl-Free Magnesia and Magnesia 2642.

The curvature is in such a direction that it indicates too much adsorption in the second layer. Figure 3 shows that at a relative pressure of about 0.5 the isotherms are above the BET $n = \infty$ plots. The assumption in the derivation of the BET equation that the heat of adsorption in the second layer is equal to the heat of liquefaction is probably not a close enough approximation for the adsorption of nitrogen on magnesium oxide.

In most cases this curvature introduces an uncertainty in the position of the best straight line which allows the v_m to be obtained with a precision of only ±5% as shown in Figure 4. The value determined in this manner is not necessarily the correct one since it disagrees with those obtained by other methods.

In order to obtain the surface area of the adsorbent from v_m, it is necessary to assign an area to the adsorbed nitrogen molecule. A wide variety of values for this area have been recommended by various authors (19) and a choice is very difficult. In most of this work the value selected by Harkins and Jura for porous solids (15.25 sq. Å) has been used.

In an attempt to find a method calculating the surface area of active magnesia which was more adaptable to the data, the recent method of Harkins and Jura (19) was applied. Their approach makes use of the equation:

$$\log p/p_0 = B - (A/v^2) \qquad (3)$$

where the slope of this equation gives the area according to the equation:

$$\text{Area} = 4.06\ (A)^{1/2}. \qquad (4)$$

The plot of Equation 3 for Magnesia 2642 is shown in Figure 5. This method appears also to be unreliable for area determination of active magnesia because the linear portion of the plot extends at best from 0.2 to 0.5 relative pressure. Harkins and Jura recommend that their method be applied only if the linear region extends from 0.1 to 0.7 relative pressure. These authors have suggested that a better fit for their equation is frequently obtained at lower

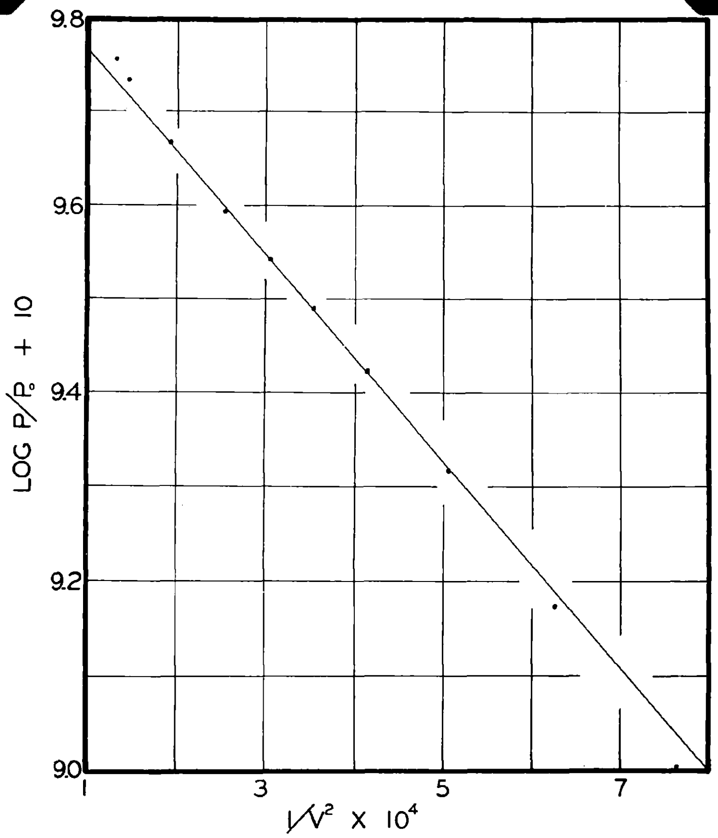

Figure 5.

Harkins-Jura Plot for Magnesia 2642.

temperatures. In order to check this possibility a nitrogen adsorption run was made on Magnesia 2642 at -201.0°C. These data showed no improvement in the linearity of the Harkins-Jura plot.

Because of the difficulties found in evaluating areas by Equations 1 and 3, v_m values were estimated by the B Point method suggested in the earlier work of Emmett and Brunauer (10). These values which are the volumes corresponding to lower extremities of the central linear portions of the isotherms are given in Table I. If the area of the nitrogen molecule is taken as 15.25 sq. Å, the value recommended by Harkins and Jura (19) for porous solids, these B Point values give the areas tabulated in Table I. These B Point areas are in good agreement with the BET areas and, except for the granular magnesias, with those determined by the Harkins and Jura plots as shown in Table I. B Point areas are used in further discussions in this paper.

The surface areas tabulated in the last column of Table I were calculated from the Iodine Numbers of Table VI in Appendix B. This was done by assuming close packing of solid iodine on the surface and using the area of the iodine molecule (21.2 sq. Å) calculated from the gram molecular volume by the method of Emmett and Brunauer (14). The areas calculated from Iodine Numbers are lower than those obtained from nitrogen adsorption by about 35%. The relative order obtained for the commercial active magnesias is, however, correct.

Table I
Surface Areas
Sq. meters/g.

		B Point		BET		
Expt. No.	Grade*	v_m cc. (STP)	Area (N_2:15.25	Area sq. Å)	H-J Plot	From I_2 No.
6	Cl-Free	48.3	198	230	209	134
42	2642	34.5	142	154	140	96
21	2652-S	34	140	146	127	93
9	2652	30	123	125	109	83
10	2641	18	74	71	81.5	48.5
5	2661 1/2	8	33	33.5	32.9	19.8
8	2665	8	33	31	31.4	15.9
13	2661	0.18	0.73	0.79	0.74	2.5

*See Appendix B.

AREA DETERMINATION BY PREFERRED POSITION THEORY

A new approach to the assignment of areas to the adsorbed nitrogen and iodine molecules brought the results presented in Table I into much better agreement. If the case of the adsorption of a single nitrogen molecule on the face of a magnesia crystal is considered, it is undoubtedly true that one of the several possible positions with respect to the ions on the crystal face will give the adsorbed molecule greater stability than any other. This reasoning is substantiated by the work of Orr (21) who calculated the energy of an argon atom adsorbed over various parts of a 100 crystal face of the cubic cell of potassium chloride. It is reasonable to believe that the first unimolecular layer of adsorbate is formed by molecules orienting themselves over as many of these positions of maximum stability as possible without overlapping. On the basis of this picture it is possible to calculate the area effectively covered by a molecule adsorbed on a crystalline surface.

The possible positions of maximum stability on the face of a magnesia crystal fall into two categories according to their spacing patterns. The first is exemplified by the centers of unit cells which were found by Orr (21) to be the most stable positions for argon on potassium chloride. On a magnesia crystal these positions are arranged in a square pattern with intervals of 2.10 Å. The second category includes positions directly over one of the kinds of ions such as the magnesium ion where a molecule near the size of nitrogen attains the closest packing into the crystal face. These positions are also found in a square configuration, but the interval is 2.97 Å.

From geometric considerations it may be shown that the effective areas of adsorbed spherical molecules on a square pattern of stable positions can have only the values given by the expression $n^2a^2(m^2 + 1)$ sq. Å. The quantity a is the distance between preferred positions, and n and m are integers which may have minimum values of one and zero respectively. A molecule having an effective area given by this expression must have a diameter equal to or less than the square root of this expression and greater than the square root of the next smaller area obtainable by adjusting the values of m and n. Application of this principle to the surface of a magnesium oxide crystal gives the results tabulated in Table II.

Table II

Effective Areas of Spherical Molecules
Adsorbed on Magnesium Oxide.

First Category a = 2.10 Å		Second Category a = 2.97 Å	
Molecular Diameter Å	Effective Area Sq. Å	Molecular Diameter Å	Effective Area Sq. Å
0 - 2.10	4.42	0 - 2.97	8.83
2.10 - 2.97	8.83	2.97 - 4.20	17.67
2.97 - 4.20	17.67	4.20 - 5.94	35.33
4.20 - 4.70	22.08	5.94 - 6.65	44.16
4.70 - 5.94	35.33	6.65 - 8.40	70.66
5.94 - 6.30	39.75	8.40 - 8.91	79.49
6.30 - 6.65	44.16	8.91 - 9.40	88.33
6.65 - 8.40	70.66		
8.40 - 8.66	75.08		
8.66 - 8.91	79.49		
8.91 - 9.40	88.33		

As shown in Table II, if the adsorbed nitrogen molecule is assumed to be nearly spherical, it must effectively cover 17.67 sq. Å no matter which type of position it prefers. This area assignment for the adsorbed nitrogen molecule is 5% higher than the highest assignment previously reported in the literature and is specific for adsorption on magnesium oxide.

The case of the adsorption of iodine on magnesia is more complex since the assumption of a spherical molecule for iodine is not reasonable as it is for nitrogen. The size and shape of the iodine molecule were approximated using the I-I bond distance of 2.66 Å as given by Pauling (22) and the atom radius of 1.77 Å as given by Clark (23). These figures indicate that the adsorbed iodine molecule should be a dumb-bell shaped figure 3.54 Å wide and 6.20 Å long. The order of magnitude of these dimensions may be readily checked by dividing the gram molecular volume by Avogadro's number. If the volume thus obtained is assumed to be in two laterally joined cubes, then the dimensions of a long side of the molecule are found to be 3.5 by 7.0 Å. It may be shown that it molecules of these dimensions lie flat on the 100 face of a magnesia crystal and if they all take the same position with respect to the ions in the crystal surface, then with the closest possible packing each iodine molecule will effectively occupy 35.33 sq. Å of the solid surface.

The most logical position for an adsorbed iodine molecule is a combination of the two which are most highly recommended for smaller molecules. In this position the center of the iodine molecule is placed over the center of a unit lattice cell and the two nuclei fall almost exactly over the adjacent magnesium ions. Figure 6 shows the closest possible packing of iodine molecules in such positions.

It is of interest to note that if the iodine were adsorbed as atomic rather than molecular iodine, then an iodine atom would behave in the same manner as described for nitrogen molecules, and the area occupied per iodine molecule would again be 35.33 sq. Å.

If the values deduced here for the areas of the nitrogen and iodine molecules are used in place of those obtained by older methods, the areas of the active magnesias as determined by nitrogen and iodine adsorption are in much better agreement as shown in Table III. This table shows that the new area assignments bring the areas determined by iodine adsorption into very much better agreement with the nitrogen areas, especially those determined by the B Point method. Some discrepancies are to be expected for two reasons.

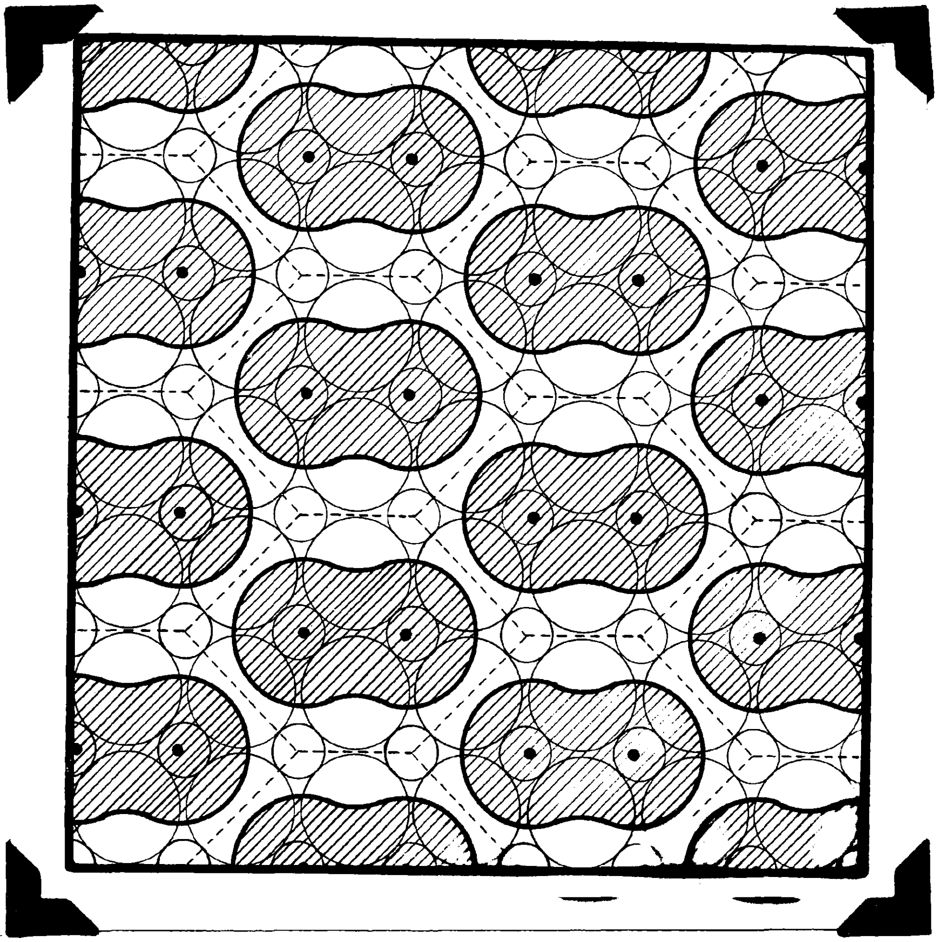

Figure 6.

Orientation of Iodine Molecules on the Surface of Magnesium Oxide.

Table III
New Surface Areas
Sq. meters/g.

- - - - -

Expt. No.	Grade*	B Point (N_2 : 17.67 sq. Å)	Iodine (35.33 sq. Å)
6	Cl-Free	229	223
42	2642	164	159
21	2652-S	162	155
9	2652	142	138
10	2641	85.5	80.6
5	2661 1/2	38.2	46.6
8	2665	38.2	26.5
13	2661	0.85	4.2

* See Appendix B

First, the active magnesias used are not pure magnesium oxide; and, as has been shown earlier, the presence of impurities causes the iodine adsorption to be too small. This effect should make the observed nitrogen areas slightly larger than those from iodine adsorption. Second, the samples used for the iodine adsorptions and for the nitrogen adsorptions were not strictly comparable since no degassing is used in the determination of iodine adsorption. Considering these difficulties, the results of Table III by the two methods appear to be in excellent agreement.

The theory of preferred positions also gives an interesting picture of the second adsorbed layer. Since the first layer is not close-packed, the molecules of the second layer can fit partly into the spaces between the molecules of the first layer and approach the face of the solid. This tendency should increase the heat of adsorption in the second layer above the heat of liquefaction. This would explain the deviation of our data from the BET theory.

The assumption of preferred positions allows an interesting prediction to be made. If this theory holds, the volume of gas adsorbed at the completion of the unimolecular layer would be a function not only of the area of the molecule but also of the arrangement of the preferred positions. Thus, according to Table II, nitrogen and argon molecules with their diameters of about 3.8 and 3.5 Å, as determined from density of liquid and solid respectively, should effectively cover the area of magnesia crystal face. In other words the volumes of nitrogen and argon required to complete the first unimolecular layer should be equal according to the theory of preferred positions.

On the basis of the usual assumption of close-packing in the first layer, a different result would be predicted. Table IV shows a compilation of areas for nitrogen and argon molecules derived from various sources. These areas do not agree well, but they leave no doubt that the argon molecule has an area about 20% smaller than that for nitrogen. On the basis of close-packing it would be predicted that a 20% greater volume of argon must be adsorbed to complete the monolayer. On the other hand, if the same volume of both argon and nitrogen is required to complete the first layer, then the theory

Table IV

Areas of Adsorbed Nitrogen and Argon Molecules

- - - - - -

Method	Nitrogen	Argon	Ratio
Gas Viscosity	7.8	6.5	0.84
Van der Waals constants	7.8	6.8	0.87
Thermal conductivity of gases	9.8	6.4	0.66
*Gram molecular volume (Emmett & Brunauer's method)	16.2	12.8	0.79
		Average	0.79

*(Nitrogen assumed liquid and argon solid since these are the physical states of these elements at the temperature of adsorption.)

of preferred positions is substantiated.

Nitrogen and argon adsorption measurements were made on the same sample of Magnesia 2642, and the isotherms are presented in Figure 7. The v_m's were determined by the B Point method by two observers and were found to agree within two percent with the value for nitrogen tending to be high instead of low**. This experiment demonstrated again, therefore, that the concept of preferred positions gives a more reliable picture of adsorption on active magnesia than does the concept of close-packing. It is to be expected that the theory of preferred positions will find wide application as the basis for assignment of effective areas to adsorbed molecules.

HEAT OF ADSORPTION

The isosteric or differential heats of adsorption of nitrogen on Magnesia 2642 were evaluated from four isotherms measured in the temperature range 72.26 to 79.40°K. The isotherms obtained at the two extreme temperatures are presented in Figure 8. From the isotherms at constant volumes adsorbed, plots of ln p versus 1/T were obtained. The slopes of these straight lines gave the heats of adsorption according to the Clausius-Clapeyron equation.

When the heats of adsorption are plotted against the volumes adsorbed, the curve given in Figure 9 is obtained. These heat values are net heats of adsorption; that is, they represent differences between the total differential heat of adsorption at any particular volume adsorbed and the heat of liquefaction. A steady decrease occurs until the unimolecular layer is passed. The leveling off is followed by another sharp decrease at an adsorbed volume corresponding to the second plateaus in the isotherms. The curve then decreases gradually toward the heat of liquefaction which is the zero ordinate in Figure 9.

**BET plots were also used (in spite of some uncertainty due to curvature.) These calculated v_m's showed that the value for argon was less than five percent in excess of that for nitrogen.

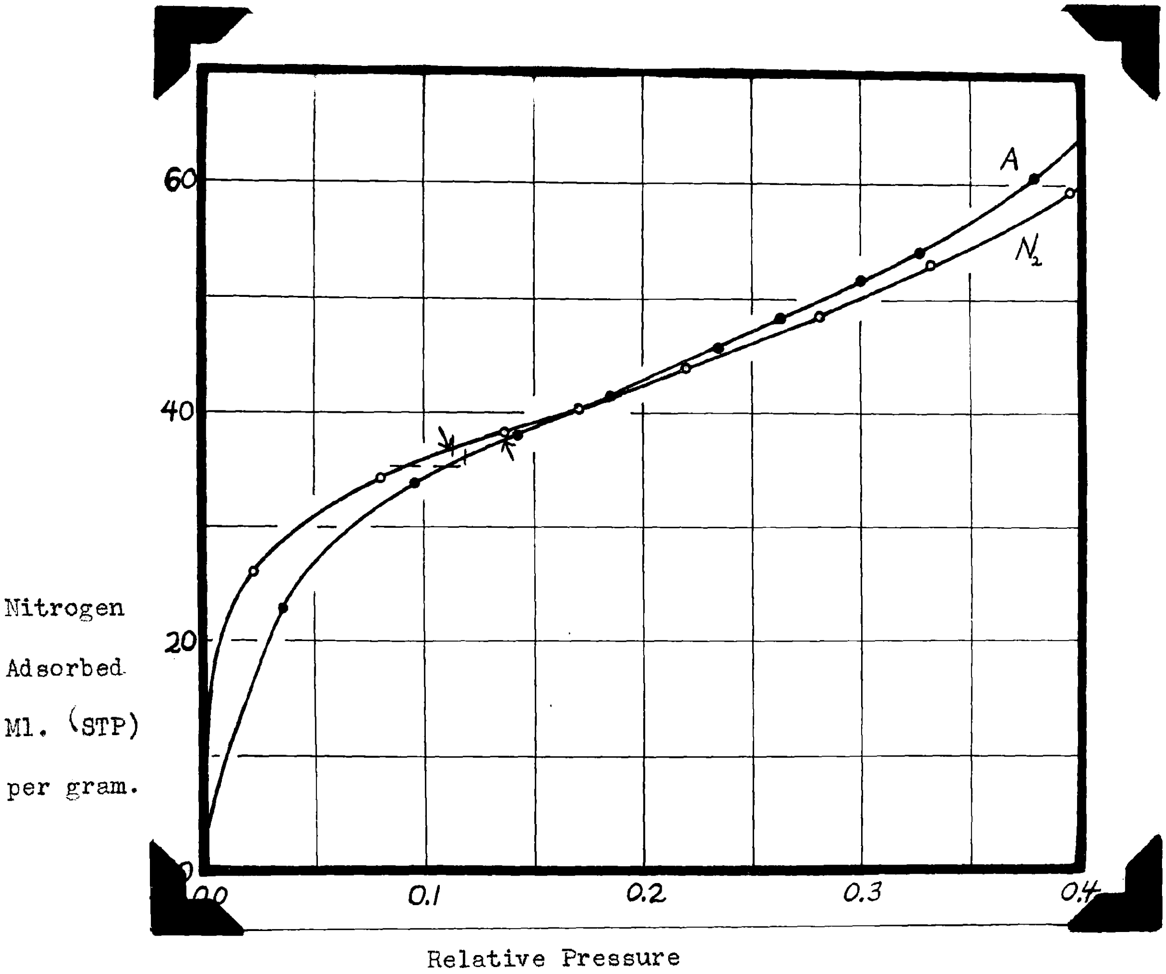

Figure 7.

Isotherms of Nitrogen and Argon Adsorption on Magnesia 2642.

Key

B Point Vm
— Observer 1.
| Observer 2.

↖ BET Vm

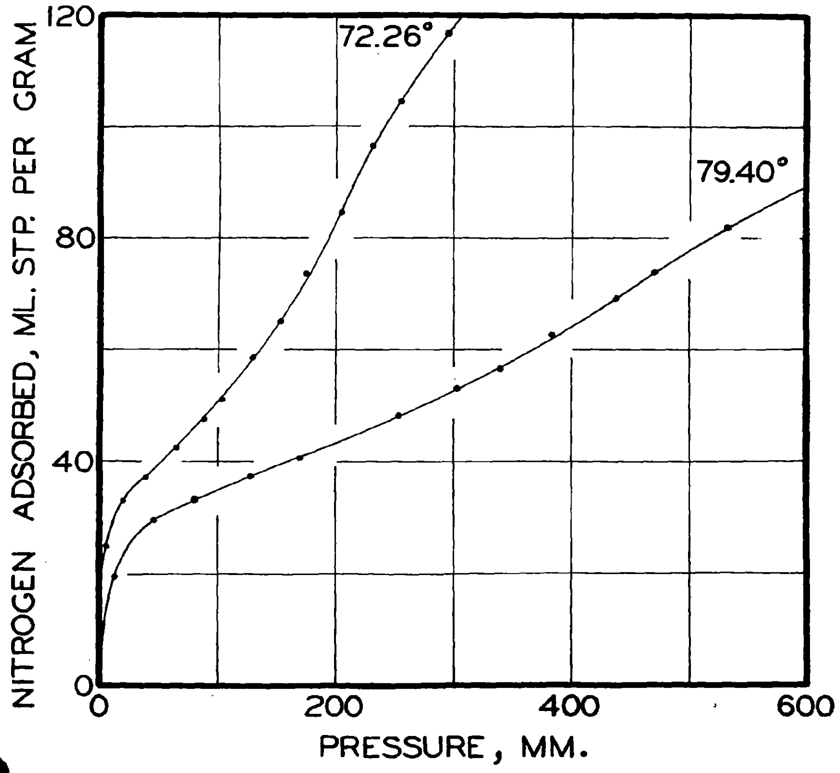

Figure 8.

Nitrogen Adsorption on Magnesia 2642 at
the Extreme Temperatures.

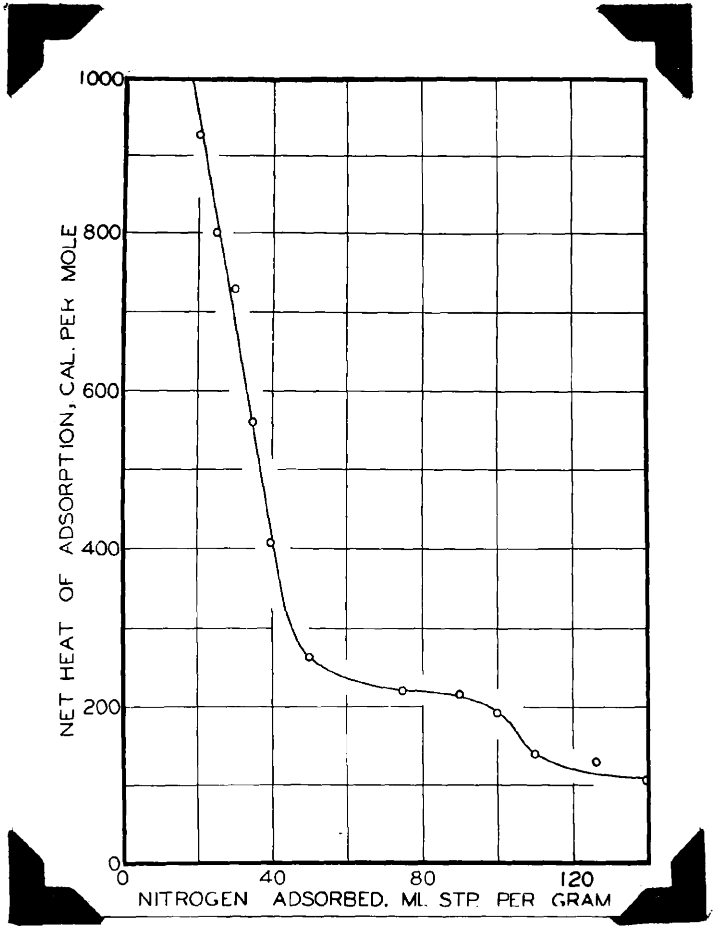

Figure 9.

Net Heat of Adsorption of Nitrogen on Magnesia 2642.

The second sharp break in the heat curve corresponding to the second plateau in the isotherms is in accord with the earlier suggestion that this marks the point where the smaller pores of uniform size are completely filled. The heat of adsorption is almost entirely the heat of liquefaction after the pores of uniform size are filled.

POTENTIAL THEORY

In connection with the heat of adsorption it is of interest to apply the adsorption theory of Polanyi (14,24). If this theory applies to the adsorption, an isotherm at one temperature may be calculated from that determined at another temperature. The variation of the net heat of adsorption with the amount adsorbed can also be obtained. The theory, however, does not permit the calculation of surface areas.

According to the potential theory the Polanyi potential

$$\mathcal{E} = RT \ln \frac{Po}{p} \qquad (5)$$

plotted against the volume of liquid adsorbed corrected for compressibility and temperature expansion ϕ should give a line independent of the temperature. As a matter of fact, the Polanyi potential plotted against the uncorrected volume adsorbed, Figure 10, gives curves at the four temperatures which coincide. Similar agreement was noted for the curves for nitrogen on iron catalysts (14). Coincidence of these so-called affinity curves means that the differential heat of compression for the adsorbed nitrogen is negligible. This means in turn that the Polanyi potential represents closely the net heat of adsorption. Comparison of Figures 9 and 10 shows a striking similarity between the two curves; within the limit of experimental error the isosteric heats of adsorption and the heats of adsorption obtained from the potential theory agree. Similar breaks occur in the two curves in the neighborhood of v = 100 ml. nitrogen adsorbed.

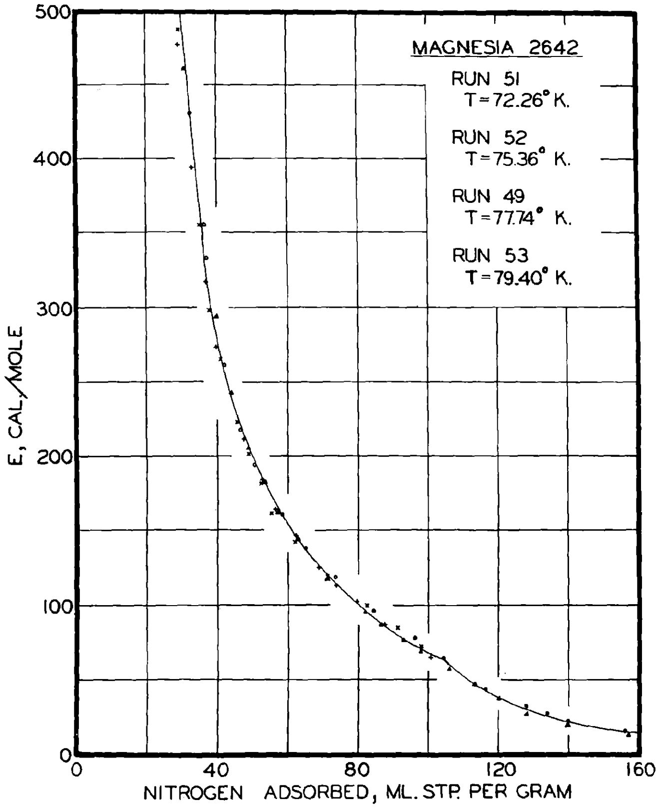

Figure 10.

Application of Potential Theory to Magnesia 2642.

Although limited in its usefulness, it appears that the potential adsorption theory applies to the adsorption of nitrogen on active magnesia.

PORE STRUCTURE OF ACTIVE MAGNESIA

As was mentioned earlier, the isotherms of the adsorption of nitrogen on active magnesia show both Type II and Type IV characteristics. These isotherms can also be considered as the sums of Type II and Type IV isotherms. This implies that active magnesia contains two kinds of adsorbing surface differing in adsorptive properties. The surface giving the Type IV isotherm is considered to be contained in small capillaries of uniform radius and parallel walls, but the surface giving the Type II isotherm is probably a more random structure. It is evident that the extents of these two kinds of surface must be of the same order of magnitude.

On the basis of these observations and the fact that magnesium oxide occurs in simple cubic crystals, a structure has been hypothesized to explain the shape of the observed adsorption isotherms. This structure consists essentially of plates of a checkerwork of cubic holes and crystallites. Four faces of each crystallite are within the holes and make up the surface which contributes the Type IV character to the isotherms. The other two faces of each crystallite are in the outer surface of the plate, and these faces make up the surface on which Type II adsorption takes place. The plates may be arranged in a random order with respect to one another and form between them the relatively large crevices and capillaries in which condensation takes place at high relative pressures.

This idealized structure gives a satisfactory qualitative explanation for the observed shape of the adsorption isotherms and can be substantiated by independent methods. Thus, Büssem and Köberich (25) concluded from a study of the X-ray diffraction pattern, obtained from the dehydration product of a single crystal of magnesium hydroxide, that the minute magnesia crystallites present were oriented with corresponding faces parallel.

Further supporting evidence is presented in Figure 11, which is a reproduction of a photograph of one of the hypothesized plates taken with the aid of an electron microscope by L. Marton of Stanford University (26).

The approximate size of the holes in the plates may be obtained with the aid of Kelvin's Equation for capillary condensation (14). This equation relates the radius of a capillary to the relative pressure at which condensation takes place.

$$r = \frac{2\sigma V \cos\theta}{RT \ln p_o/p} \qquad (6)$$

In this equation r is the capillary radius, σ the surface tension, V the molar volume, θ the angle of wetting, and the other letters have their usual significance. Using this equation and the relative pressure at which the second plateau is most nearly horizontal, the diameter of the holes is found to be about 50 Å.

- SUMMARY -

The adsorptions of nitrogen and argon from the vapor phase and of iodine from solution have been measured on magnesia samples of various activities.

The surface areas of the magnesias have been shown to range from less than one to more than two hundred square meters per gram.

The nitrogen adsorption isotherms are mixed Type II and Type IV.

This mixture has been explained on the basis of a structure for active magnesia consisting of plates of checkerwork of cubic holes and crystallites.

The assumption of preferred positions rather than close-packing in the first unimolecular layer has been shown to give greatly improved correlation of the data.

The effective areas of both the adsorbed nitrogen and argon molecules

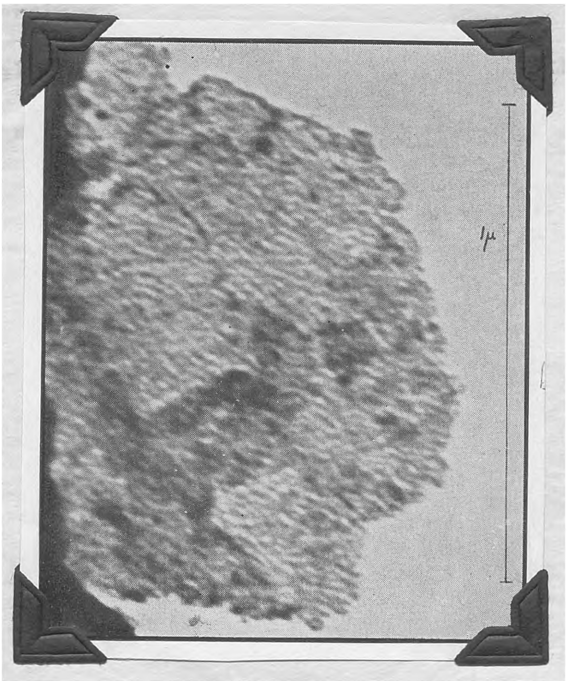

Figure 11.

Electron Photomicrograph of Plate in Active Magnesia.

on magnesium oxide have been found to be 17.67 sq. Å while the area for iodine is 35.33 sq. Å.

Iodine number determination has been established as a quick method for the determination of the area of magnesium oxide.

The differential heat of adsorption of nitrogen on active magnesia has been determined.

The potential theory has been shown to apply to the adsorption of nitrogen on active magnesia.

APPENDICES

APPENDIX A

Gas Adsorption Apparatus: Construction and Operation

The gas adsorption apparatus was built specifically for the measurement of surface areas and pore structures by the adsorption of nitrogen at the temperature of liquid nitrogen. The apparatus, however, can be readily adapted to the measurement of the adsorption of other gases and at other temperatures. It is similar to the apparatus described by Pease (27) and by Emmett and Brunauer (10), but involves certain improvements.

The apparatus is diagrammed in Figure 12. It is mounted on a supporting frame, six feet high and six by two feet wide, consisting of wooden platforms at top and bottom, supported by two inch pipe at the four corners and half inch steel rods in the center portion to which the glassware is clamped.

The 25 mm. glass tube "Header" forms the exhaust tube leading to the evacuating system, designated part A in the diagram of Figure 12. The McLeod Gage is on the line beyond the first Liquid Air Trap so that mercury vapor does not reach the sample during degassing. A McLeod Gage has been found to register the same pressure whether connected at the point indicated or at the other end of the Header.

In part B the adsorption measuring devices are grouped together. The volume adsorbed is measured by means of a standard 50 ml. Burette, air-jacketed with room temperature air. A tube parallel to the Burette joins the Burette below the calibration (as in a burette made to feed at constant pressure). Therefore, when the levels in the Burette and tube are adjusted to the same level, the pressure of the gas in the Burette is the barometric pressure. This feature eliminates a mercury leveling bulb and tube. The pressure of the gas being adsorbed is measured on the Pressure Manometer open to the high vacuum line on the high side. On the low side the mercury must

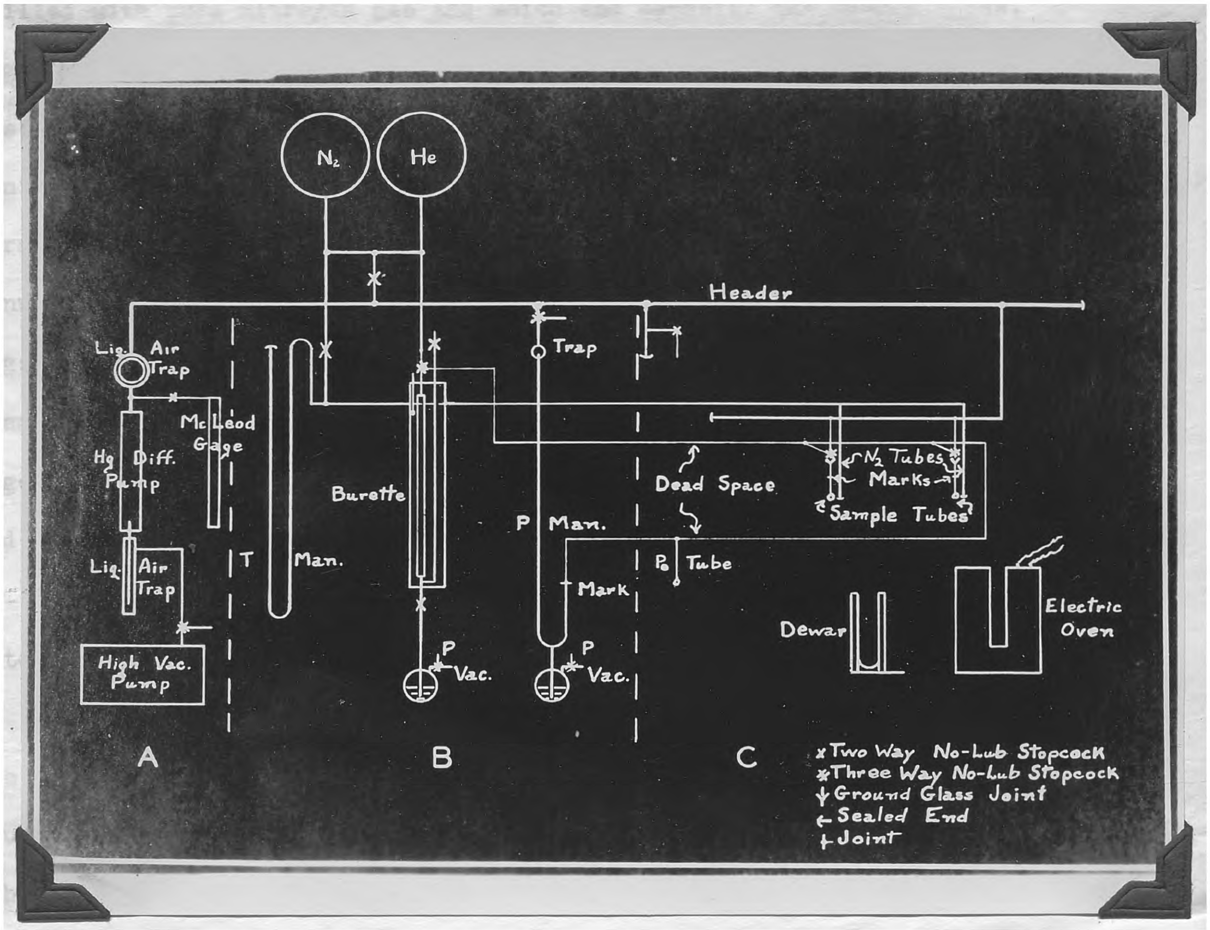

Figure 12.

Diagram of Adsorption Apparatus.

be brought to the same Mark for each reading so that the same volume is enclosed from the Pressure Manometer through the Sample Tube to the Burette. The Temperature Manometer is connected to tubes (the Nitrogen Tubes) which are filled with pure nitrogen gas and which end opposite the Sample Tubes. During the course of the adsorption study when one Sample and Nitrogen Tube set is immersed in the impure liquid nitrogen bath in the Dewar, some of the pure nitrogen gas condenses in the bottom of the Nitrogen Tube. Then, the Temperature Manometer readings made during the adsorption study give a continuous record of the change in the vapor pressure, p_o, above the liquid nitrogen in the Nitrogen Tube and, thus, of the change in the temperature of the sample. The temperature of the sample changes slightly because the impure nitrogen bath in the Dewar becomes more impure with age. Narrow mirrors are placed behind the manometers for ease in reading.

Above part B the 5 liter gas storage bulbs and the connections from them to the system are indicated.

Part C shows the Sample Tubes. There are two of them so that one sample may be degassed while adsorption is being measured on the other sample. The tubes are detachable and consist of 10/30 standard tapered glass joints attached to a bulb made from 10-12 mm. tubing by a short length of 8 mm. tubing. A Mark at a convenient point near the center of this tubing indicates the level to which the liquid nitrogen bath is brought and maintained during the adsorption run. The standard tapered joint fits a male joint connected to both the Header (for degassing) and to the Burette and Pressure Manometer line (for adsorption), by means of a three-way stopcock. The Sample Tubes have stoppers made from male joints so that they can be closed when detached from the rig for weighing. An Electric Furnace containing a silica tube is used for degassing and a Dewar flask is used for the liquid nitrogen bath.

Usual technique is reported to involve only one measurement of p_o, the vapor pressure of liquid nitrogen at the bath temperature. At the end of the adsorption measurements the Dewar is moved from the sample tube to the p_o Tube. The sudden warming of the sample releases large amounts of nitrogen some of which condenses in the p_o Tube so that p_o can be measured on the Pressure Manometer. Because of the drift in p_o during the course of long runs as described above, the Temperature Manometer system, which is merely a nitrogen thermometer, has been added and the p_o Tube is used only for check purposes. For technical reasons explained later on, volumes adsorbed are plotted against relative pressures, p/p_o, rather than against the pressure.

The tubing connecting the Pressure Manometer to the Burette and connecting from this line to the Sample Tubes is 1 mm. bore and as short as conveniently possible. This tubing, together with the space above the adsorbent in the sample tube, is called the Dead Space. It represents the volume of gas introduced which is not adsorbed. The chief source of error in the adsorption measurements is due to the error in its measurement and maintenance at the same value. Therefore, it is easy to see why it is that the level of the mercury in the Pressure Manometer and the level of the liquid nitrogen in the Dewar must be brought to the same Marks before each set of readings. The volume of the Dead Space is measured before each adsorption run by introducing known volumes of pure helium from the Burette and measuring the pressures on the Pressure Manometer. Helium is not adsorbed at the temperature of liquid nitrogen.

The helium must be purified on filling the helium bulb by very slowly passing it over activated coconut charcoal at the temperature of liquid nitrogen. The nitrogen is used as purchased at a stated purity of greater than 99.9%.

Stopcocks in the high vacuum system are No-Lub ground and the plungers are coated with a very thin but complete film of Apie$_z$on M stopcock grease, J. G. Biddle Company, Philadelphia. A somewhat heavier grease, Cenco's Vac. Sealing Compound, is used on the ground glass joints at the Sample Tubes.

Measurement of Adsorption

The operation of the apparatus may be divided up as follows: preparation of the sample, determination of the Dead Space, and measurement of the gas adsorbed.

Preparation of the sample begins with the weighing of one-tenth to five-tenths of a gram of sample into the Sample Tube. The sample is covered with a wad of glass wool to prevent "boiling" the sample into the high vacuum line during degassing. The Tube is reweighed to determine the weight of the glass wool. The male member of the joint is then greased with a small amount of heavy grease near the top of the joint and the Sample Tube is put in place. The sample is then degassed at 1×10^{-5} mm. Hg pressure while heated by the Electric Furnace. Except for the study of the effect of temperature and time variations on the extent of the surface, the magnesias have been treated at 250°C. for one hour. The temperature and time of degassing should be such that as much of the adsorbed air and water as possible are removed without appreciable increase or decrease in the surface area. During the heating period it is important that stopcocks and the joints be kept cool, if necessary by wrapping with a damp cloth, so that grease or vapors from the grease do not get onto the sample.

Determination of the Dead Space is made by drawing about 15 ml. of helium, measured at atmospheric pressure, into the Burette. With the Sample Tube, plus Nitrogen Tube immersed in the liquid nitrogen bath up to the Mark, about 3 ml. of the helium are bled from the Burette into the empty Dead Space. The volume of gas left in the Burette is read and the Pressure Manometer is read after the lower arm is adjusted to the Mark. Three ml. more are bled in and the readings are taken as before. This procedure is repeated until four or five sets of readings are obtained. From the readings an average value for the ml. of gas occupying the Dead Space per mm. reading on the Pressure Manometer is obtained. To examine the consistency of these results and to check the purity of the helium (the impurities would probably be adsorbed), the STP accumulative total volumes bled into the Dead Space are plotted against the pressures. The points should fall on a straight line passing through the zero point of the graph.

Due to changes in room temperature, bath temperature, barometric pressure, sample volume and Sample Tube, the Dead Space must be determined for each run.

Measurement of the gas adsorbed may begin after the helium is evacuated and nitrogen is drawn into the Burette. The same procedure is followed between the STP accumulative total volume obtained with the nitrogen and that obtained with the helium for the same Pressure Manometer reading is the amount of the nitrogen adsorbed at that pressure. For determining only the surface area, four or five of these values between relative pressures of 0.05 and 0.35 are required. Surfaces of most adsorbents are believed to be completely covered with a monolayer at a relative pressure of the order of 0.1. For measurement of the complete isotherm the measurements can be extended to p_o. Upon reversal of the adsorption, some adsorbents--and magnesia falls into this class--exhibit hysteresis loops, i.e., upon measuring the isotherm from the p_o end by slowly taking the gas back into the Burette the points fall above the original isotherm.

Because the procedure of adding adsorbate or removing adsorbate described above involves approach to the equilibrium pressure from the high or the low side respectively, the addition or removal of the gas must be made in small increments. Otherwise the points would fall above the true curve on ascending and below on descending the hysteresis loop.

During the adsorption run the drift in the p_0 is measured periodically on the Temperature Manometer.

The final step is to obtain the final sample weight. This is accomplished by removing the Sample Tube from the rig, wiping off the grease with a cloth dampened with benzene, allowing the benzene to evaporate, and immediately thereafter closing with the stopper and weighing. Volumes of gas adsorbed per gram are calculated on the basis of final sample weights. From the initial and final weights, the ignition loss on degassing can be calculated.

The adsorption isotherms are plotted as milliliters (STP) of nitrogen adsorbed per gram of sample against the relative pressure, p/p_0.

After the degassing operation, it takes two to three hours to obtain the data for area determinations and about the same amount of time to complete the calculations. About twelve to fifteen hours are required to measure a complete isotherm including the hysteresis loop. Equilibrium for each point is usually not attained until fifteen or twenty minutes after the last portion of gas is added or removed. As the relative pressure approaches one, equilibrium may not be obtained for several hours.

APPENDIX B

Commercial Production Methods

The essential operations for the production of the active magnesias investigated here involve first the production of lime by the calcination of oyster shells. Bitterns remaining after sodium chloride has been separated from sea-water by solar evaporation are treated with this lime to precipitate the more insoluble magnesium hydroxide. Since the bitterns contain sulfate, a portion of calcium chloride obtained by the reaction of the lime with the magnesium chloride in the bitterns is recycled, thus precipitating the sulfate as calcium sulfate, before the reaction with the lime. The magnesium hydroxide, which is precipitated in as granular a form as possible at about 50°C. with mild mechanical agitation, is washed counter-currently in Dorr thickeners. The washed sludge is filtered in a rotary vacuum filter and fed into the stack end of a rotary kiln. The details of these operations have been adequately described by Seaton (28).

The rotary kiln is fired counter-current with gas or fuel oil. By trial, the temperature of a thermocouple located at a point between the feed and discharge end of the kiln is correlated to the activity of the magnesia discharged from the kiln. Subsequent production is then carried out by maintaining the temperature of this intermediate couple at the desired level. The two factors varied to control the final activity are temperature and time of retention in the kiln. Pertinent data for the commercial grades of active magnesia are given in Table V, and analyses are given in Table VI.

Table V

Production Conditions

Grade	Intermediate Couple % of Kiln Length From Discharge End	°C	Retention Time Hours
2641	50	750	0.5
2642	50	700	0.5
2652-S	50	625	0.5
2652			
2661	45	600-700	2
2665	31	300-400	4

Magnesias 2652-S and 2661 1/2 are experimental grades. Magnesia 2652 is a granular variety, -8 to +48 mesh, obtained by burning magnesite ore, hydrating and reburning; it was included in these studies for comparison with the sea-water varieties. Magnesia 2652-S is a comparable granular grade from sea-water. Magnesia 2661 is considered to be a "chemical" rather than an active grade, but is included also for purposes of comparison. Chloride-free magnesia is made by carbonation of magnesium hydroxide precipitated from sea-water bittern. The chlorides are then washed out of the resulting hydrous carbonate before calcination.

Table VI

Properties of Samples

Grade	2641	2642	2652-S	2652	2661 1/2	2661	2665
*Iodine No.	76	150	146	130	44	4	25
Ignition Loss,%	8.7	6.8	7.2	7.0	1.4	0.1	6.5
Typical Chemical Analysis, % Ignited Basis							
SiO_2	0.8	Same	Same	0.8	0.7	Same	0.6
Fe_2O_3	0.3			0.4	0.2		0.2
Al_2O_3	0.4	as	as	0.3	0.3	as	0.2
CaO	1.5			2.6	1.3		1.2
MgO	96.5	2641	2641	95.9	97.4	2661 1/2	97.2
Approximate Particle Size, microns		5			2	3	
Bulk Densities lb./cu.ft.	27	30	42	46	22	52.5	14.5

* See Appendix C.

APPENDIX C

Iodine Number Determination

Procedure:

1. Weigh to the nearest milligram a 2-gram sample of material.

2. Transfer to a clean, dry, 100 ml., oil sample bottle.

3. Add 100 ml. ±0.5 ml. of 0.1000 N iodine in carbon tetrachloride. The carbon tetrachloride must be free from traces of sulfur or carbon disulfide.

4. Stopper the bottle with a cork protected with tinfoil and shake vigorously in a suitable shaking device for exactly 30 minutes.

5. Allow to settle 5 minutes and pipette 20 ml. of the clear solution into a 250 ml. Erlenmeyer flask containing 50 ml. of 0.03 N KI in 75% ethanol.

6. Titrate with standard 0.05 N sodium thiosulfate. A sharp endpoint can be obtained without the use of starch indicator.

7. Calculate the iodine number by subtracting the milliliters of thiosulfate used from the milliliters of thiosulfate required for 20 ml. of the original iodine solution and multiply the results by two hundred fifty times the normality of the sodium thiosulfate.

$$I_2 \text{ No.} = 250 \times N_{thio} \times (\text{ml. thio for blank} - \text{ml. thio for titration})$$

This value is reported to the nearest unit only.

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VITA

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