[CONTRIBUTION FROM THE PORTLAND CEMENT ASSOCIATION, CHICAGO, ILLINOIS]

# Modification of the Brunauer–Emmett–Teller Theory of Multimolecular Adsorption

BY GERALD PICKETT

The Brunauer–Emmett–Teller equations[1] for multimolecular adsorption have been found to be in good agreement with experimental data for relative vapor pressures in the range 0.05 to 0.35. In some cases agreement is good over a greater range, but it is rarely good for relative vapor pressures greater than 0.50. Moreover, as pointed out by Brunauer, according to the B. E. T. equations, the capillary spaces available for adsorption in porous adsorbents are never much more than half filled even at saturation pressure. In general the spaces actually fill when exposed to saturation pressure. The primary purpose of this paper is to show that if one of the B. E. T. assumptions is replaced by a more logical assumption, the resulting equations: (a) will indicate complete filling of the spaces at saturation, (b) will be in good agreement with experimental data over a greater range of vapor pressures than the B. E. T. equations, (c) are simpler than the B. E. T. equations. The paper also shows that an equation that is both readily usable and in good agreement with all examined experimental data for the whole range of relative vapor pressures can be obtained if the assumption is made that the size-distribution of the larger capillaries is exponential.

In any theoretical development that is to be applied to physical phenomena simplifying assumptions are always necessary. The choice of assumptions should be based upon both the accuracy with which they appear to represent the actual phenomena and the simplicity they introduce. The choices made by Brunauer, Emmett and Teller in their original derivations are considered to be satisfactory for the most part. Though their assumptions that the adsorbing surface is plane, that all parts of the surface have equal activities, and that the range of van der Waals forces of the adsorbent is limited to the first layer of the adsorbate could be replaced by others more in accord with the facts, such replacements would complicate the analysis without materially increasing accuracy.

In this paper all the simplifying assumptions made by Brunauer, Emmett and Teller except one will be accepted. The assumption to which exception is taken is the implicit one that so far as evaporation is concerned the final layer of adsorbate on an element of surface is fully exposed regardless of the number of layers on any adjacent element of surface. This implicit assumption follows from their assumption on page 311 of reference 1 "that $a_1$, $b_1$, and $E_1$ are independent of the number of adsorbed molecules already present in the first layers" and the additional assumptions on page 312 that $E_2 = E_3 = E_i = E_L$ and $b_2/a_2 = b_3/a_3 = b_i/a_i = g$.

It is believed that this particular assumption in the B. E. T. theory is primarily responsible for the observed lack of agreement between their equation and experimental data at the higher relative vapor pressures. With such an assumption in the theoretical development it is impossible for the derived equations to indicate complete filling of the capillary spaces at any vapor pressure less than infinity. On the other hand, all that is necessary to provide for complete filling is to introduce an assumption that takes into account a decrease in probability of escape from an elemental area covered with *n* layers (the maximum number possible in the limited space) as adjacent elemental areas also become covered with *n* layers and leads to the result that there can be no evaporation from an area covered with *n* layers when *all* adjacent areas are also covered with *n* layers.

The assumption that is made by the present writer is that for the *n*th (final) layer the ratio $b_n/a_n$ is equal to $g(1 - x)$, instead of $g$ only, where $x$ is the relative vapor pressure. No change is made in the other $b/a$ ratios. On this basis the B. E. T. relation (equation 21 of ref. 1)

$$S_i = xS_{i-1} = x^{i-1}S_1 = cx^iS_0$$

is still applicable for $i$ less than $n$ but for $i$ equal to $n$ the relation becomes

$$S_n = \frac{x}{1-x} S_{n-1} \tag{1}$$

When these values are substituted into the expressions (see equations 13 and 14 of ref. 1)

$$A = \sum_{i=0}^{n} S_i \text{ and } \frac{v}{v_0} = \sum_{i=1}^{n} iS_i$$

the result is

$$A = S_0 + cS_0\left[x + x^2 + \ldots x^i + \ldots x^{n-1} + \frac{x^n}{1-x}\right]$$

and

$$\frac{v}{v_0} = cS_0\left[x + 2x^2 + \ldots ix^i + \ldots (n-1)x^{n-1} + \frac{nx^n}{1-x}\right]$$

These equations reduce to

$$A = S_0 \frac{1 - x + cx}{1 - x} \tag{2}$$

and

$$\frac{v}{v_0} = \frac{cxS_0(1 - x^n)}{(1 - x)^2} \tag{3}$$

respectively.

From equations 2 and 3 and the relation $v_m = v_0A$ there is obtained

$$\frac{v}{v_m} = \frac{cx(1 - x^n)}{(1 - x)(1 - x + cx)} \tag{4}$$

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[1] Stephen Brunauer, P. H. Emmett and Edward Teller, THIS JOURNAL, 60, 309 (1938).

instead of equation B of the B. E. T. development, which is

$$\frac{v}{v_m} = \frac{cx}{1 - x} \cdot \frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (c - 1)x - cx^{n+1}} \tag{B}$$

At corresponding vapor pressures in the lower range equations 4 and B give about the same results, but at higher vapor pressures equation 4 indicates more adsorption than equation B. As $x$ approaches unity, $v/v_m$ approaches $n$ in equation 4, indicating complete filling of the capillary spaces at saturation, whereas as $x$ approaches unity $v/v_m$ approaches $\frac{n + 1}{2(1 + 1/cn)}$ in equation B, indicating only a little more than half filling of the capillary spaces at saturation.

Of importance is the fact that according to the foregoing development the fraction of bare surface is a function of the factor $c$ and the relative pressure $x$ only, whereas in the B. E. T. development the fraction of bare surface is a function of $n$ as well as $c$ and $x$. That is, from equation 2 above

$$\frac{S_0}{A} = \frac{1 - x}{1 - x + cx} \tag{2a}$$

and from the B. E. T. development

$$\frac{S_0}{A} = \frac{1 - x}{1 - x + cx - cx^{n+1}} \tag{B$_1$}$$

According to equation 2a the fraction of bare surface becomes infinitesimally small as $x$ approaches unity whereas according to equation $B_1$ the fraction of bare surface approaches the finite value of $1/(1 + cn)$ as $x$ approaches unity. Moreover, from equation 2a and the relation $S_i = cx^iS_0$ for $i$ less than $n$ it follows that

$$\frac{S_i}{A} = \frac{cx^i(1 - x)}{1 - x + cx} \tag{2b}$$

indicating that the fraction of surface covered with exactly $i$ layers is independent of $n$ and becomes infinitesimally small as $x$ approaches unity, whereas according to the B. E. T. development

$$\frac{S_i}{A} = \frac{cx^i(1 - x)}{1 - x + cx - cx^{n+1}}$$

which approaches $c/(1 + cn)$ as $x$ approaches unity. Furthermore, from equations 1 and 2b, $S_n$ becomes equal to $A$, or all the space becomes filled when $x$ becomes unity.

It seems reasonable to the present writer that the height of the "ceiling"[2] limiting the number of layers should have very little effect on any of the ratios $S_0/A$, $S_1/A$ . . . $S_i/A$ as long as $i$ is somewhat smaller than $n$. For example, consider the adsorbent surface to consist of two adjacent plane surfaces $A_1$ and $A_2$. Assume that there is no limit to the number of layers that can be accommodated over $A_1$ but that a "ceiling" limits to $n$ the number of layers over $A_2$. Under these conditions, it appears that the fractions of bare surface and those covered with one, two, etc., layers should be practically the same under the ceiling as out in the open, as is indicated by equations 2a and 2b.

Instead of attempting to correct the ratio $b_n/a_n$ to take into account the reduced probability of escape from the $n$th layer as more surface is covered with $n$ layers, the following two assumptions might have been made:

(1) The height of ceiling has no effect on the fractions of the surface that are bare and covered with one, two, . . . $n - 1$ layers;

(2) All parts that would have had more than $n$ layers without a ceiling have just $n$ layers.

With these assumptions equation 4 is again obtained. That is, if the process of condensation and evaporation is considered to take place according to the B. E. T. theory as though no ceiling were present but in computing the quantity adsorbed that quantity which would be in layers beyond the $n$th is omitted, the result is

$$\frac{v}{v_m} = \frac{cS_0\left[\sum\limits_{i=1}^{n} ix^i + n\sum\limits_{i=n+1}^{\infty} x^i\right]}{S_0\left[1 + c\sum\limits_{i=1}^{\infty} x^i\right]}$$

which reduces to equation 4.

Figure 1 is an illustration of the better agreement with experimental data afforded by equation 4. This is Fig. 3 of the original B. E. T. paper with a superimposed dashed curve representing the modified theory.

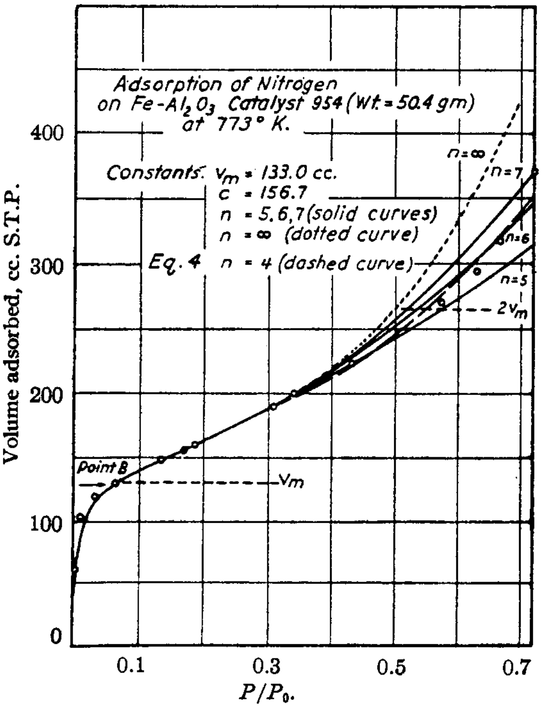

Fig. 1.—Figure 3 of Brunauer–Emmett–Teller paper with curve from eq. 4 superimposed.

The following form of equation 4 is suitable for

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[2] The "ceiling" may be thought of as one half the distance separating two parallel elements of surface.

the determination of the constants $v_m$, $c$, and $n$ from experimental data

$$\frac{x(1-x^n)}{v(1-x)} = \frac{1}{cv_m} + \frac{c-1}{cv_m}x \qquad (4a)$$

Data given by Deitz and Gleysteen[3] for adsorption of nitrogen on three different carbonaceous adsorbents were analyzed by means of equation 4a with the results shown in Fig. 2.

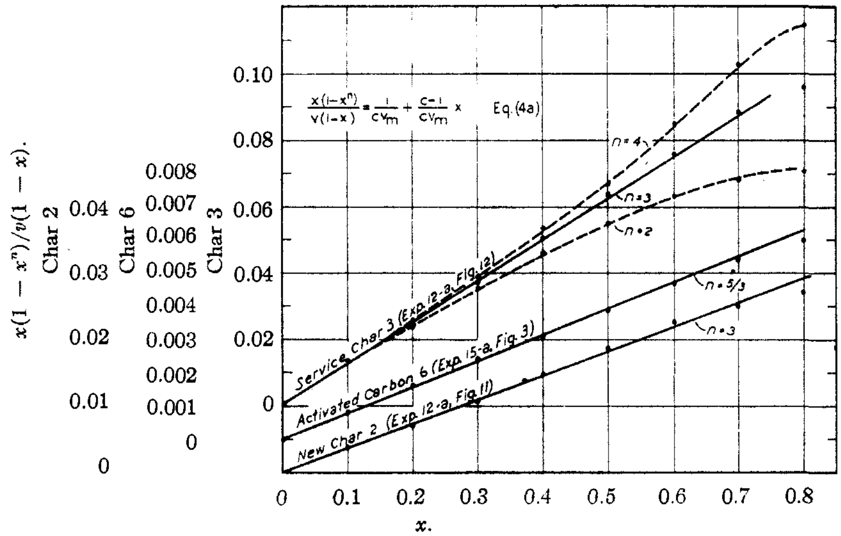

Fig. 2.—Data given by Deitz and Gleysteen plotted according to equation 4a.

When the best values of $n$ were used and the quantity $x(1-x^n)/v(1-x)$ as obtained from experiment was plotted against $x$, a linear relation up to about 0.7 for $x$ was found for each adsorbent. This means that equation 4 or 4a was in agreement with the data up to that value of the relative pressure. On the other hand, as shown by Figs. 11, 12 and 13 of the paper by Deitz and Gleysteen, equation B of Brunauer, Emmett and Teller agrees with the same data only up to, not over, 0.5 for $x$.

As shown in Fig. 2 for Service Char 3 the curve through the plotted points curves upward if the selected value of $n$ is too high and downward if too low. The best value of $n$ is determined by trial. The constants $c$ and $v_m$ are determined from the slope and intercept of the best straight line in the usual manner.

The modification here proposed does not result in any appreciable change in the experimental values of $c$ and $v_m$ from that obtained from the B. E. T. equations. The differences if any would result from the fact that more points are available for selecting the best straight line.

## New Equations for Porous Adsorbents in which a Fraction of the Spaces Are Relatively Large

The equations discussed above were based on the assumption that adsorption takes place on plane surfaces, or in the space between two plane, parallel surfaces. In view of this obvious oversimplification, the failure of the equations to fit experimental data over the whole pressure range is to be expected.

To account for a variation in size of the capillary spaces Brunauer, Emmett and Teller proposed a generalized equation (equation D, page 313 of ref. 1) based on the assumption that the total surface $A$ consists of the separate surfaces, $A_1$, $A_2$, . . . $A_i$ on which a maximum of 1, 2, . . ., $i$ layers, respectively, can be accommodated. Such a generalized equation is not of practical use because of the large number of undetermined factors $A_1/A$, $A_2/A$ . . . $A_i/A$ in addition to $v_m$ and $c$.

An equation will now be derived that is simple enough to be of practical use and flexible enough to give good agreement with experimental results for the full range of relative vapor pressures. The equation is based on the assumption that the number of layers on a part of the surface is limited to $n$ and that more than $n$ layers can be accommodated on the rest of the surface, the fraction of the surface accommodating a given number of layers being related to the number exponentially.

**Derivation of Equation.**—It is assumed that:

(1) On a fraction, $\beta$, of the total surface a maximum of $n$ layers can be accommodated.

(2) $dA/di$ is proportional to $e^{-\alpha i}$ for the remaining surface where $dA$ is the portion of surface on which from $i$ to $i + di$ layers can be built and $\alpha$ is a constant such that the total volume of adsorbate is accounted for.

(3) Equation 4 holds for any one element of the surface.

From these considerations one obtains

$$v = \frac{v_m cx}{(1-x)(1-x+cx)}\left\{\beta(1-x^n) + (1-\beta)\int_{i=n}^{\infty}\frac{dA}{A}(1-x^i)\right\} \qquad (5)$$

or after substituting for $dA$ and $A$

$$v = \frac{v_m cx}{(1-x)(1-x+cx)}\left\{\beta(1-x^n) + (1-\beta)\frac{\int_n^{\infty}(1-x^i)e^{-\alpha i}\,di}{\int_n^{\infty}e^{-\alpha i}\,di}\right\} \qquad (5a)$$

When integrated equation 5a becomes

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[3] Victor R. Deitz and Leland F. Gleysteen, *J. Research Natl. Bur. Standards*, **29**, 191-225 (1942), RP 1496.

$$v = \frac{v_m c x}{(1 - x)(1 - x + cx)} \left\{ \beta(1 - x^n) + (1 - \beta)\left[1 - \frac{x^n}{1 - (\log_e x)/\alpha}\right]\right\} \quad (6)$$

Upon setting $v = v_{\max}$ for $x = 1.0$ it is found that $\alpha = (1 - \beta)/(n_{av} - n)$ where $n_{av}$ has been written for $v_{\max}/v_m$. When this value of $\alpha$ is substituted in equation 6, the result is

$$v = \frac{v_m c x}{(1 - x)(1 - x + cx)} \left\{ \beta(1 - x^n) + (1 - \beta)\left[1 - \frac{x^n}{1 - [(n_{av} - n)\log_e x]/(1 - \beta)}\right]\right\} \quad (7)$$

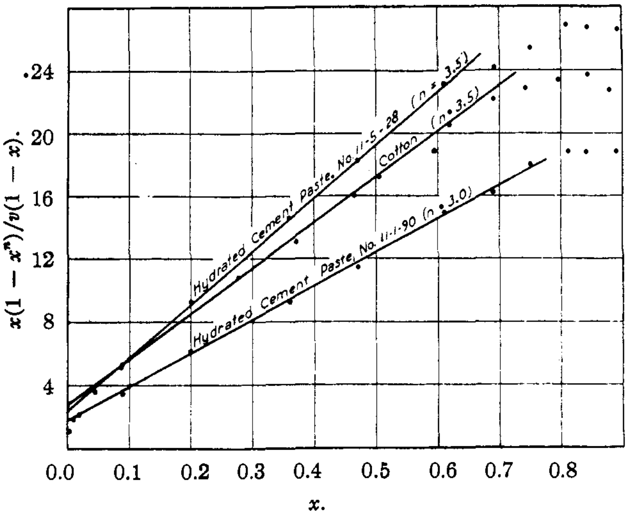

Fig. 3.—Plots of $x(1 - x^n)/v(1 - x)$ *versus* $x$ used for determining $v_m$, $c$ and $n$.

Figure 4 shows adsorption curves for water on hydrated portland cement pastes[4] and on cotton fiber.[5] The points are from experimental data; the curves were computed from equation 7 using the indicated values for the constants. The constants $v_m$, $c$, and $n$ were obtained from plots of equation 4a as shown in Fig. 3. Since $n_{av} = v_{\max}/v_m$, $n_{av}$ was, of course, readily obtained after $v_m$ was found. $\beta$ was selected by trial so as to give good agreement at the higher relative vapor pressures.

It is realized that although the agreement is good the assumptions that were made in deriving equation 7 are largely speculative and therefore the constants probably do not have exactly the meanings ascribed to them in the derivation. However, some basis for the assumptions as far as applicability to hydrated pastes of portland cement is concerned is given by experiments made in this Laboratory. These experiments indicate that the spaces in hydrated paste may be thought of as belonging in two categories: (1) spaces that are, in total amount and size distribution, characteristic of the gel substance, and (2) spaces that are extraneous to the gel substance. The extraneous spaces evidently represent residues of the original space in which the gel was laid down; it is thought of as a capillary system permeating the porous gel.

The residual space in hardened pastes can be practically eliminated by a suitable choice of original water–cement ratio and conditions of curing. The adsorption isotherms from pastes so prepared can be represented, at least up to about $x = 0.95$, by equation 4 with $n$ at 3 or 3.5. For samples of higher total porosity equation 4 approximates the data to the extent indicated above in the discussion of the data from Deitz and Gleysteen.

### Type IV and Type V Isotherms

Equations 4 and 7 are not applicable for the higher relative vapor pressures of adsorbents that give Type IV or Type V isotherms. The B. E. T. equations for these isotherms[6] can be modified in the manner here indicated. If variation in size of capillary space is considered, the modification becomes very complicated; but if variation in size of capillary spaces is not considered, the modification is relatively simple. For example, when so modified, equation 46 on page 169 of ref. 5 becomes:

$$v = \frac{v_m c\left[x(1 - x^n) + \frac{g - 1}{2} n x^n (1 - x)\right]}{(1 - x)\left[1 - x + c\left(x + \frac{g - 1}{2} x^n\right)\right]} \quad (8)$$

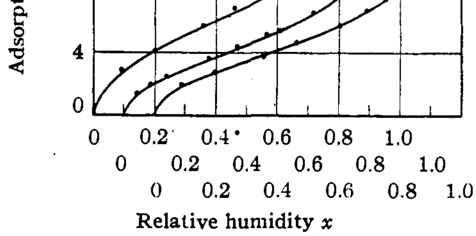

Fig. 4.—Examples of fitting experimental data with equation 7:

| Curve | Adsorbent | Constants used in eq. 7 | | | | |
|---|---|---|---|---|---|---|
| | | $v_m$ | $c$ | $n$ | $n_{av}$ | $\beta$ |
| A | Portland Cement Paste, 11-5-28 | 0.0433 | 12.8 | 3.0 | 4.37 | 0.95 |
| B | Cotton | .0319 | 11.2 | 3.5 | 7.20 | .85 |
| C | Portland Cement Paste, 11-1-90 | .0275 | 15.1 | 3.5 | 8.76 | .85 |

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(4) Unpublished data, Research Laboratory of the Portland Cement Association.

(5) A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **40**, T439 (1924).

(6) Stephen Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Princeton University Press, London, 1943.

This equation, like equation 4, gives $v/v_m = n$ when $x = 1.0$.

**Acknowledgment.**—The author is indebted to Mr. T. C. Powers, Manager of the Basic-Research Division of the Portland Cement Association, for suggesting and directing this investigation.

## Summary

By modifying the Brunauer–Emmett–Teller theory of multimolecular adsorption to take into account a decrease in probability of escape of molecules in the $n$th layer as more of the surface is covered with $n$ layers, equations have been derived that are simpler in form and are in better agreement with experimental data than the original Brunauer–Emmett–Teller equations.

CHICAGO, ILLINOIS RECEIVED APRIL 23, 1945

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

# The Preparation and Hydrolysis of Manganese Carbide ($Mn_3C$)

BY WARD R. MYERS AND W. P. FISHEL

Since the early work of Moissan[1] on the hydrolysis of manganese carbides, in which he reports the reaction $Mn_3C + 6H_2O \rightarrow 3Mn(OH)_2 + CH_4 + H_2$, very little work has been done dealing with the chemical properties of carbides of manganese.

This work is a portion of a program dealing with the preparation and chemical properties of metallic carbides. $Mn_3C$ has been prepared and its hydrolysis with water and acids studied.

## Experimental

Products agreeing very closely in composition with the theory for $Mn_3C$ (93.22% Mn, 6.78% C) were prepared (1) by heating metallic manganese with sugar charcoal, and (2) by the reduction of $MnO_2$ with an excess of sugar charcoal.

**Preparation of Carbide.**—Metallic manganese prepared by alumino-thermic reduction was mixed with graphite and heated to 1600° in an Acheson graphite crucible in a carbon resistor furnace. The charge was held in a molten condition for thirty minutes and was then allowed to cool in the furnace to room temperature. The gray crystalline product was ground to pass a 200-mesh sieve and was purified by the methods described later. From all samples prepared in this manner a ferro-magnetic substance could be separated. It was found to consist of 77.6% manganese, 3.76% carbon, 8.0% aluminum and iron, with 10.7% insoluble in nitric acid. The non-magnetic portions contained traces of iron and aluminum. Sample A was prepared in this manner.

In order to eliminate iron and aluminum, other sources of manganese were sought. Carbide was prepared by reducing purified manganese dioxide with sugar charcoal in a magnesium oxide lined graphite crucible heated in a high frequency induction furnace. This method was successful but very troublesome and time consuming.

The method finally adopted was that of heating electrolytic manganese with an excess of sugar charcoal. The manganese was obtained as a fine, gray powder by distilling the mercury from a mercury–manganese amalgam which was made by the electrolytic reduction of manganous sulfate using mercury as the cathode. The manganese powder and charcoal mixture was moistened with glycerol and pressed into pellets. These pellets were placed in an Acheson graphite crucible lined with magnesium oxide and heated in the induction furnace to near the boiling point of the melt (about 1800° at 750 mm.) and held at this temperature for twenty minutes. The power was then cut off and the crucible allowed to cool to room temperature in the furnace. This required about thirty minutes. Sample B was prepared in this way.

All of the carbide prepared according to the method described for sample B contained approximately 7.3% combined carbon, which is 0.5% too high for $Mn_3C$. It was found that if the temperature of the melt be held just above its melting point (about 1300° at 750 mm.) the combined carbon of the melt approached the value required by the formula $Mn_3C$. Southard and Moore[2] report a transformation in $Mn_3C$ at 1037°. In practice the temperature of the melt was reduced to and held at the melting point for three hours after which time it was allowed to cool to room temperature. Sample C was prepared in this manner.

**Purification Methods.**—All samples were crushed in a diamond mortar and ground to pass a 200-mesh sieve. The powdered material contained free carbon as graphite. This excess carbon was removed with difficulty and in no case was its removal complete. Proper precaution was used to protect the material, as far as possible, from hydrolysis during the purification.

The use of tetrabromomethane, as suggested by Ruff and Gestern,[3] was unsatisfactory. The heavy liquid did not wet the product and is in itself very difficult to remove. Repeated elutriation with carbon tetrachloride followed by anhydrous ether was fairly successful. The most satisfactory results were obtained by blowing the fine carbon out of the carbide samples with a current of dry air. Three Erlenmeyer flasks were connected in series by glass tubing in such a way that the air entered the first, passed through the second, and out through an exit in the third. The powder was placed in the first flask and a stream of dry air passed through the flasks under a pressure that permitted only the finest of the material to be blown out the exit of the third flask. Fractions collect in the second and third flasks during the operation. Sample C originally contained 9.44% total carbon. This was reduced to a 7.32% carbon by an air separation. The light material collecting in the third flask contained 16% total carbon. The free carbon is apparently present as graphite which is impossible to separate completely.

It was impossible to prevent some hydrolysis during grinding and purification. This accounts for the presence of some manganese oxide in the sample.

### Analytical Methods

**Manganese.**—Manganese was determined by Cunningham and Coltman's[4] bismuthate method. It conformed to that recommended by the Bureau of Standards for the determination of manganese metal and in ferro-manganese.

**Total Carbon.**—Total carbon was determined by combustion in the manner ordinarily employed for ferro-manganese. The samples were burned at 1150–1200° using ingot iron as an accelerator. The carbon dioxide was absorbed in ascarite.

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(1) Moissan, *Compt. rend.*, **116**, 349 (1893); **122**, 421 (1896).

(2) Southard and Moore, THIS JOURNAL, **64**, 1769 (1942).

(3) Ruff and Gestern, *Ber.*, **46**, 400 (1913).

(4) Cunningham and Coltman, *J. Ind. Eng. Chem.*, **16**, 58 (1924)