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

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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 nth 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.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

The Preparation and Hydrolysis of Manganese Carbide (Mn_3C)

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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 ferromanganese. 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)

Combined Carbon.—The combined carbon was determined by hydrolyzing samples of the carbide with water and passing the evolved gases through a silica tube containing copper oxide at 650°. Following the silica tube there were two Lundell bubblers containing a solution of chromium trioxide in concentrated sulfuric acid. The carbon dioxide formed was either absorbed in ascarite or converted to barium carbonate according to the method of McFarlane and Gregory.[5] The flask in which the hydrolyses were carried out was constructed from a 250-cc. Erlenmeyer flask by sealing a ground glass joint on to the neck of the flask. The insert of the joint carried a small water-cooled condenser, a dropping funnel for introducing water into the reaction flask, and an air inlet which extended almost to the bottom of the flask when the insert was in place. These were all attached to the insert by glass seals. An exit tube for the gases near the top of the condenser was connected through a small mercury trap to the silica tube. One branch of a carbon dioxide-free air line was connected to the air inlet leading into the flask and the other to the top of the dropping funnel. Phosphoric acid was used as a lubricant for the ground glass joint.

In making an analysis the flask was dried and put in place and carbon dioxide free air was passed through the entire apparatus until it was free from carbon dioxide. The apparatus was then sealed off with pinch clamps, the flask was removed and a weighed sample of the carbide was placed in it. The flask was again put in place, the pinch clamps were removed and a slow stream of carbon dioxide free air was circulated through the apparatus. Cold, recently boiled, distilled water was now introduced in the flask from the dropping funnel. Near the end of the reaction the flask was heated in a water-bath and the air stream increased somewhat in order to sweep all of the evolved gas through the train. The carbon dioxide was weighed directly if ascarite had been used or was weighed as barium carbonate had the ammoniacal barium chloride method been employed. Careful blank determinations were made for both methods.

Free Carbon.—The carbon remaining in the reaction flask after water hydrolysis was taken as being the free carbon present in the sample. The contents of the flask were filtered in a previously ignited silica thimble which carried an asbestos mat. The residue was washed repeatedly with water, dried at 90° for one hour, and ignited at 900° in the combustion furnace. The carbon dioxide formed was absorbed in ascarite. In all cases the combined carbon by evolution and the residual or free carbon equaled the total carbon by combustion. It was, therefore, assumed that the carbon combined with Mn as Mn_3C could be determined by evolution.

Hydrolysis with Hydrochloric Acid.—Studies of the behavior of the carbide samples with hydrochloric acid solutions were carried out in the same apparatus employed for the determination of combined carbon by water hydrolysis. Regardless of the strength of acid used it was found that only a part of the combined carbon was liberated as gaseous hydrocarbons and the amount of free carbon was greater than with water hydrolysis. However, the carbon by evolution and the free carbon did not equal the total carbon. The difference was assumed to be due to liquid hydrocarbons formed on acid hydrolysis. An oily film formed in the evolution flask. The percentage of hydrogen in the evolved gas was higher and varied with the rate of reaction.

Gas Analysis.—All analyses were made in an apparatus similar in design to that described in the Bureau of Mines Bulletin 197.[6] The gas samples were collected over water in such a way that they were contaminated with not more than traces of air. Samples were analyzed for illuminants, hydrogen, carbon monoxide, methane and ethane. No effort was made to identify the unsaturated constituents except that qualitative tests for acetylene were negative. Ethane and methane were determined together by combustion and the percentage of each calculated by the usual equations. The reason for reporting the saturated hydrocarbons as methane and ethane is simply that no single hydrocarbon or other combination could account for the residual gas after the combustion of hydrogen; and the contraction and carbon dioxide resulting from its combustion.

Summary of Results

In Table I the partial analysis of samples A and B and the complete analysis of the sample C are given. It will be noted that the total for sample C lacks 0.79 of equaling 100%. Further, the combined carbon is below the theoretical for Mn_3C. From its behavior with very dilute hydrochloric acid (a small residue was obtained which proved to be Mn_3O_4 and a faint odor of chlorine was detected) it was assumed that the sample contained an oxide of manganese. The manganese required to combine with 6.48% carbon to form Mn_3C is 88.96%. If this be subtracted from the total manganese the difference is 2.58%, which is equivalent to 3.57% Mn_3O_4. On this basis the proximate analysis of sample C is as follows

Mn_3C	95.44%
M_3O_4	3.57
Fe	0.19
MgO	0.07
SiO_2	0.09
Free C	0.83
Total	100.19%

In order to obtain additional information concerning the composition of the material, about 10 g. of sample C was hydrolyzed completely with water at room temperature in a flask fitted with an escape valve which excluded air. Manganous hydroxide formed, and a film which had all the appearance of finely divided graphite. After the reaction was complete, enough dilute hydrochloric acid to dissolve the manganous hydroxide was added. It was then filtered through a glass fiber crucible. The black residue obtained was shown to be carbon by combustion in oxygen. No manganese oxide residue remained after combustion.

The evidence indicates that the samples of carbide are Mn_3C contaminated with an excess of carbon in the form of graphite, similar to graphite found in gray cast iron. The oxides of manganese

TABLE I

COMPOSITIONS OF CARBIDE SAMPLES

	Sample A	Sample B	Sample C
Manganese	90.52%	92.10%	91.54%
Total carbon	7.09	7.57	7.32
Combined carbon by H_2O hydrolysis		7.30	6.48
Free carbon		0.28	0.83
Iron			.19
Magnesium oxide			.07
Silica			.09
Total	97.61%	99.67%	99.21%

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(5) McFarlane and Gregory, *Chem. News*, **94**, 133 (1906).

(6) Bureau of Mines Bulletin 197, Sampling and Examination of Mine Gases and Natural Gas.

found in the samples resulted from some hydrolysis during grinding and purification.

It might be argued that lower oxides of manganese were also present. The excess carbon present before grinding; the close approach of the composition of the purified sample to the theoretical value for Mn_3C, and the known tendency for excess carbon to precipitate from molten alloys as graphite do not support this conclusion.

Sample C on the basis of 95.44% purity contains Mn 95.91% and combined carbon 6.79% which is in close agreement with the theoretical for Mn_3C.

The results of the analysis of the gas from sample C by water hydrolysis at the temperatures indicated are given in Table II. The reported values are averages of at least two determinations. In all cases the percentages were computed on a nitrogen and oxygen free basis. The volume of nitrogen and oxygen in the samples, however, rarely exceeded one per cent.

TABLE II

COMPOSITION OF GASES FROM WATER HYDROLYSIS

	Sample C, %		
	90°	40°	20°
Illuminants	3.76	3.36	3.58
Hydrogen	74.26	75.17	75.80
Carbon monoxide	0.52	0.15	0.22
Methane	15.62	12.58	13.76
Ethane	5.84	8.74	6.64

Analyses were made of the gaseous products obtained when the samples were dissolved in hydrochloric acid (sp. gr. 1.10). From sample C the gas contained 95% hydrogen. The methane/ethane ratio was practically the same as in the gas obtained by water hydrolysis.

It was previously pointed out that on treating the carbide samples with hydrochloric acid solutions only a part of the combined carbon was liberated as volatile hydrocarbons and that free carbon and liquid hydrocarbons were formed in the reaction.

A comparison of water and acid hydrolysis is given in Table III.

TABLE III

HYDROLYSIS OF SAMPLE C

Water hydrolysis

Carbon evolved, 6.48% Free carbon, 0.83%
Acid hydrolysis (HCl sp. gr. 1.10)
Carbon evolved, 2.51% Free carbon, 3.73%
Combined carbon converted to free carbon by acid 2.90%
Combined carbon converted to liquid hydrocarbons 1.07%

Discussion of Data

The observation of Ruff and Bormann[7] that carbon dissolves in manganese at temperatures above its melting point to form an alloy corresponding to Mn_3C, was confirmed in this investigation. The highest combined carbon content was obtained in sample B. This undoubtedly is very near the maximum solubility of carbon in manganese at the boiling point of the melt under atmospheric pressure, since only a few minutes were required to cool the alloy from the boiling point to the freezing point. The maximum solubility of carbon at 1525°, the boiling point of melts under 30 mm. pressure, as determined by Ruff and Bormann is 7.12%.

The gas analyses definitely point to errors in the literature and text-books as to the hydrolytic products of Mn_3C with water. No results were obtained which approached the 50% hydrogen and 50% methane reported by Moissan. The results of the gas analyses can be explained most satisfactorily in terms of the free methylene radical theory of carbide hydrolysis.

Summary

A carbide closely approaching the theoretical composition of Mn_3C has been prepared. Its water hydrolysis liberates all the combined carbon as gaseous hydrocarbons chiefly methane, ethane, and some alkenes of low molecular weight.

Acid hydrolysis promotes formation of free carbon, hydrogen, and liquid hydrocarbons.

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[7] Ruff and Bormann, *Z. anorg. Chem.*, **88**, 365 (1914).

[8] Original manuscript received February 17, 1945.