fall far short of the molal entropy of the three dimensional gas at all coverages and that they approach the entropies of the solid and liquid bulk phases only when $v \geqq v_{\mathrm{m}}$. The same observations could, of course, be made concerning the molal entropy value for nitrogen on rutile derived from the data of Morrison and Szasz.

The entropy as predicted by the B.E.T. theory is in fair agreement with the experimental entropy at a coverage defined by $v/v_{\mathrm{m}} = 1$. At all coverages less than this value, the B.E.T. theory requires entropies which diverge increasingly, as v/v_{m} becomes smaller, from the entropies obtained from experimental evidence. At the monolayer the B.E.T. theory assumes a small configurational entropy. The fair agreement of the entropy values based on the B.E.T. theory and those calculated from the experimental data at the monolayer suggests that this assumption may well be a valid one at this coverage. At lower coverages than $v/v_{\mathrm{m}} = 1$, the B.E.T. theory requires a considerable configurational entropy, because it postulates that the molecules favor all sites equally and therefore have a large choice of sites. This is seen by examining Hill's partition function for the B.E.T. theory. The factor $B!/(B - X)!X!$ in this partition function (where X molecules are adsorbed on B sites) will result in a maximum configurational entropy contribution, and is responsible for the extremely high entropies required by the B.E.T. theory at low coverages. The disagreement of the experimental evidence and B.E.T. theory at coverages less than $v/v_{\mathrm{m}} = 1$ therefore indicates that this assumption of maximum configurational entropy is not correct and the B.E.T. theory is inadequate in this region for that reason. These conclusions might be derived from considerations of heat data alone. It has been shown that the E_1 as derived from the B.E.T. theory is in good agreement with the experimental differential heat only at $v/v_{\mathrm{m}} = 1$. Therefore it may be suggested that the B.E.T. theory is valid at the completion of the monolayer, but not prior to the completion.

Summary

1. The differential heat of adsorption of nitrogen and oxygen on titanium dioxide has been determined calorimetrically at 78.5°K. The titanium dioxide used in both cases was a sample of anatase with a B.E.T. surface area of 13.9 sq. m. per g.
2. The magnitude of the heat in both cases indicates that the adsorption is van der Waals in nature. The initial increments of nitrogen showed a heat of adsorption approximately 1 kcal. per mole higher than the initial oxygen values.
3. The partial molal entropy of the adsorbed gas was determined from our experimental data for both nitrogen and oxygen adsorbed on carbon black and titanium dioxide (anatase) at 78.5°K.
4. The results show that the partial molal entropy of the adsorbed gas is less than the partial molal entropy of the bulk three-dimensional liquid or solid phases, at coverages less than a monolayer (as defined by the B.E.T. v_{m}), for all the systems investigated. At coverages greater than a monolayer, the partial molal entropy approaches the entropy of the three-dimensional liquid or solid.
5. The entropy requirements of the B.E.T. theory are shown to be incompatible with experimental evidence at coverages less than a monolayer.

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[CONTRIBUTION FROM DIVISION OF INDUSTRIAL CHEMISTRY, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION]

A Hydrous Manganese Oxide with Exchange Properties

BY A. D. WADSLEY

Although numerous attempts to form manganese dioxide by gaseous oxidation of alkaline suspensions of manganous hydroxide have been made, complete oxidation is apparently never achieved, and the products are reported to vary in composition between $MnO_{1.95}$ and $MnO_{1.60}$.[1-5] Nicholls and Walton[3] found that the oxidative products were amorphous to X-rays. Copeland, *et al.*,[5] observed the diffraction pattern ascribed to delta-MnO_2[6] on drying their preparation at 150°. Feitknecht and Marti[4] prepared an oxide varying in composition between $MnO_{1.7}$ and $MnO_{1.8}$ with a powder pattern derived from a new phase to which they gave the name manganous manganite.

In the course of an investigation of the structures and properties of the manganese oxides and minerals, the writer has had occasion to employ this method of preparation. It was found that products other than manganous manganite or delta-MnO_2 could be identified. Of these a hydrous oxide was obtained which appears not to have been described.

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(1) J. W. Meyer and R. Nerlich, *Z. anorg. chem.*, **116**, 117 (1921).

(2) J. Herman and O. Lievin, *Compt. rend.*, **200**, 1474 (1935).

(3) A. R. Nicholls and J. H. Walton, THIS JOURNAL, **64**, 1866 (1942).

(4) W. Feitknecht and W. Marti, *Helv. Chim. Acta*, **28**, 129 (1945).

(5) L. C. Copeland, F. S. Griffith and C. B. Schertzinger, *Trans. Electrochem. Soc.*, **92**, 127 (1947).

(6) H. F. McMurdie, *ibid.*, **86**, 316 (1944).

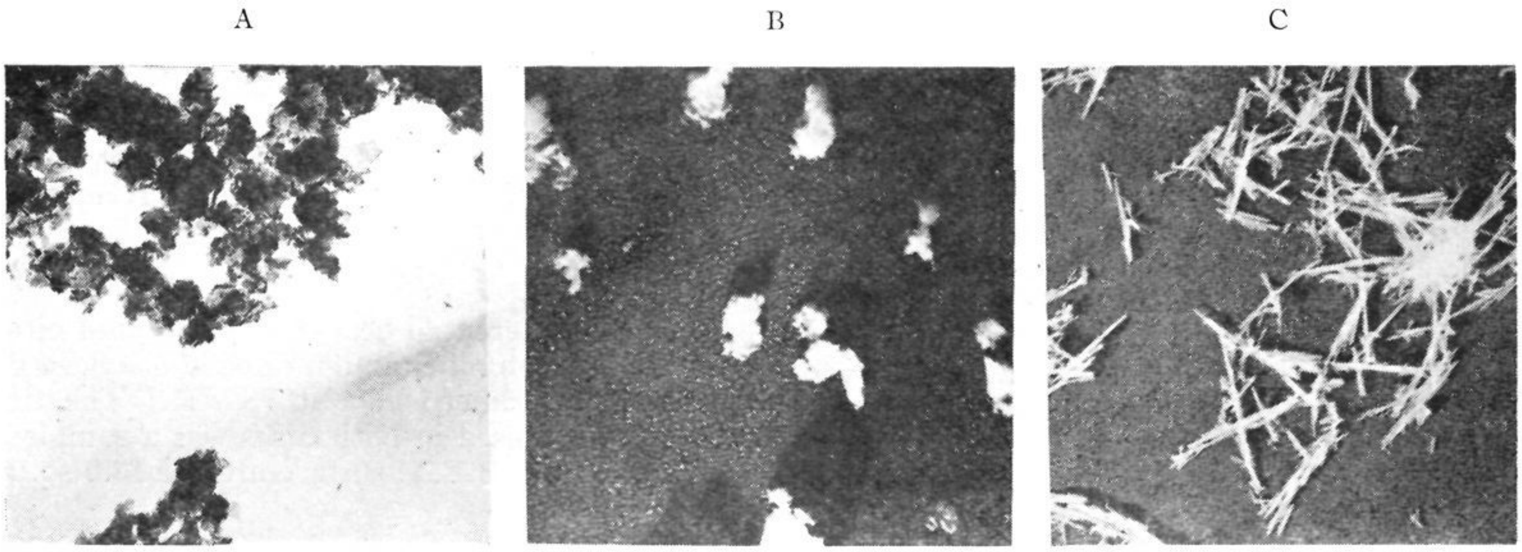

Fig. 1.—Electron micrographs: A, new hydrous oxide (× 20,000); B, manganous manganite (× 22,000), shadow cast with gold; C, δ-MnO_2 (× 22,000), shadow cast with gold.

Experimental

A cold solution of 550 g. of analytical reagent grade sodium hydroxide in 2.5 liters of water was added to a solution of 300 g. of recrystallized manganese nitrate hexahydrate in 2 liters of water. Oxygen, dispersed by means of a porous clay filter candle, was passed through the suspension of manganese hydroxide for five hours. The resulting dark brown precipitate was washed with water several times by decantation, filtered and washed further, dried at 35°, pulverized in a hammer mill and stored in a tightly stoppered bottle.

Anal. After correction for water lost by heating for one hour at 120°: MnO_2, 75.6; MnO, 11.4; Na_2O, 5.2; H_2O, 7.6; total, 99.8; density, 3.8.

X-Ray Diffraction.—The X-ray powder pattern of this substance is distinct from those of manganous manganite and delta-MnO_2 prepared by the methods of Feitknecht and Marti[4] and Copeland, Griffith and Schertzinger,[5] respectively. It is not obviously that of a mixture of any known manganese oxides, although amorphous materials if present would not be recognized from this evidence. The electron micrograph shows it to consist mainly of very thin overlapping sheets, differing sharply from those of manganous manganite and delta-MnO_2 (Fig. 1),[7] and it is on this evidence that it is treated as a unique phase. Attempts made to recrystallize the oxide were unsuccessful. Heating with dilute nitric acid, a procedure used by Glemser[7a] to obtain sharper diffraction patterns of γ-MnO_2, destroyed the structure to form γ-MnO_2. Heating with dilute sodium hydroxide solution in a stainless steel bomb at either 160° or 300° formed Mn_3O_4 (hausmannite). At the higher temperature the Mn_3O_4 was found to consist of well-defined octahedra readily visible under a low-power microscope.

Consequently the determination of crystallographic constants was attempted by an analysis of the powder pattern. The film-like nature, seen from electron micrograph, would suggest that the material possesses a marked basal plane development, and on this basis the innermost line (10 Å.) is taken as the (0001) reflection. Table I gives the measured powder pattern together with that calculated for a hexagonal cell with the dimensions: a, 8.41; c, 10.1 Å.

Table I

X-Ray Powder Diffraction Data for Hydrous Manganese Oxide

Camera radius, 14.3 cm.; FeKα = 1.937. S = strong, M = med., MW = med. weak, VW = very weak, (d) = diffuse

Estimated intensity	d	d (calcd.)	$hk\bar{i}l$ (calcd.)
S	10.0	10.1	(0001)
W	7.28	7.28	$(10\bar{1}0)$
M	5.06	5.06	(0002)
VW(d)	4.76		
W(d)	3.47	3.42	$(20\bar{2}1)$
W	3.372	3.372	(0003)
W(d)	2.50	(2.530)	(0004)
		(2.476)	$(20\bar{2}3)$
W	2.429	2.429	$(30\bar{3}0)$
W(d)	2.38	2.391	$(10\bar{1}4)$
VW(d)	2.14	2.133	$(21\bar{3}3)$
VW(d)	1.85	1.864	$(21\bar{3}4)$
MW	1.472	1.479	$(40\bar{4}4)$
W	1.420	1.431	(0007)

The presence of several (000l) lines and the diffuse nature of the few ($hk\bar{i}l$) reflections are reminiscent of the disordered structures shown by some of the clay minerals. The techniques used by clay workers to prepare halloysite complexes with large cations,[8] or to form layers of plate-like particles by sedimentation[9] have materially assisted the interpretation of their patterns. Such methods are without effect in this instance, although a modification of the former technique has successfully been applied to an examination of α$Zn(OH)_2$.[10]

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(7) The electron micrographs of manganous manganite and delta-MnO_2 were first reproduced in the *Transactions of the Electrochemical Society*, **92**, 133 (1947) by W. F. Cole, A. D. Wadsley and A. Walkley. They are reproduced by courtesy of the Editor of that Society's Journal.

(7a) O. Glemser, *Ber.*, **72B**, 1879 (1939).

(8) D. M. C. MacEwan, *Trans. Faraday Soc.*, **44**, 349 (1948).

(9) G. Nagelschmidt, *J. Sci. Inst.*, **18**, 100 (1941).

(10) D. M. C. MacEwan and O. Talib-Uddeen, *Nature*, **163**, 177 (1949).

The simplest formula which can be found from the analytical data is $(Na,Mn)Mn_3O_7 \cdot nH_2O$. This formula implies that there is an isomorphous replacement of divalent manganese by sodium, and in this preparation these ions are in the ratio 1:1. The combined water is not specified, as a precise interpretation is difficult with such a finely divided material of a hygroscopic nature. The analysis however indicates that the above formula contains between one and two molecules of water, and the density calculated for the unit cell contents $Na_2Mn_{14}O_{28} \cdot 8H_2O$ is 3.77 which compares favorably with the measured value 3.8. In what follows, this substance will for convenience be referred to as $(NaMn)Mn_3O_7$.

The Relationship to Manganous Manganite.—A dehydration curve of $(NaMn)Mn_3O_7$ showed a discontinuity at approximately 140°, and X-ray powder patterns showed that at this temperature manganous manganite is formed. The transformation is accomplished also by further oxidation in alkaline solution; by oxidation with alkaline ammonium persulfate; or simply by exposure to the atmosphere for several weeks. This suggests that the two phases are distinct, and that $(NaMn)Mn_3O_7$ is either less oxidized or more hydrated than manganous manganite. In this respect they appear to be related to each other in much the same way as the hydrated mineral halloysite is to metahalloysite. In each case the more hydrous form possesses a 10 Å. basal reflection on the X-ray diagram. The loss of some water at a low temperature causes this line to disappear and a line at about 7 Å. becomes the first major reflection.[11]

The existence of a phase intermediate between Mn_2O_3 (or MnOOH) and MnO_2 has long been suspected, but the results of early workers who described compounds of the type Mn_4O_7, Mn_5O_9, etc., are dismissed in the absence of conclusive structural evidence. In a recent review Anderson[12] suggested that if it existed, such a phase would most probably be non-stoichiometric. Manganous manganite appears to be variable in composition and it is possible that $(NaMn)Mn_3O_7$ may also behave in this way.

Formation of Metal Complexes.—The oxide $(NaMn)Mn_3O_7$ is capable of forming complexes with metal ions simply by shaking with a solution of a metal salt. Fifteen-gram samples were shaken for eighteen hours with 100 ml. of solutions each containing 10% by weight of K_2SO_4, $MnSO_4 \cdot 4H_2O$, $ZnCl_2$, $Pb(NO_3)_2$, $BaCl_2 \cdot 2H_2O$, $Al_2(SO_4)_3$, $CaBr_2 \cdot 3H_2O$, and $CuSO_4 \cdot 5H_2O$. After washing with water till free from the metal salt, each sample was filtered and dried in air at 35°. The analyses are reported in Table II.

Table II

Composition of Metal Manganese Complexes

Corrected for water lost by heating at 120° for one hour

	K	Mn	Zn	Pb	Ba	Al	Ca	Cu
MnO_2	71.4	68.6	65.9	53.3	61.8	57.9	70.0	65.4
MnO	11.9	23.2	12.3	9.3	11.8	14.0	3.6	7.5
R_2O	6.8							
RO			14.8	33.3	19.6		7.7	18.8
R_2O_3						17.9		
H_2O_{+120}	9.9	8.3	6.0	3.7	7.6	9.9	17.7	8.3
Total	100.0	100.1	99.0	99.6	100.8	99.7	99.0	100.0
Density	4.0	3.7	4.0	5.5	4.1	3.6	3.7	4.1

In each case sodium was present in amounts less than 0.05%. Treatment of these complexes with 10% sodium chloride or nitrate solution did not cause the removal of "foreign" metal or the retention of further sodium. The X-ray patterns of the aluminum, zinc and manganese derivatives closely resembled that of the untreated oxide. The patterns can be indexed on a similar basis, the crystallographic data being given in Table III. For the density calculation, the same degree of hydration as $(NaMn)Mn_3O_7$ has been assumed.

A decrease in the *c* dimension of the unit cell would seem to correspond to the ready replacement of sodium by the smaller ions of aluminum, zinc, and manganese. This suggests that the sodium ions are situated between structural units in a layer lattice of some form, the poorly developed X-ray diagram being indicative of considerable disorder.

The strong line at 10 Å. disappears from the patterns of the potassium, lead, barium, calcium, and copper derivatives. These differing in detail among themselves, resemble in a general way the pattern of manganous manganite.

It is most likely that the sodium is replaced in a manner represented by the equation $R^{n+} + n\text{Na(complex)} \rightarrow n\text{Na}^+ + \text{R(complex)}$.

More metal ions are retained than are stoichiometrically equivalent to the sodium ions replaced. However, Gruner[13] has demonstrated that the mineral cryptomelane, with the approximate formula KMn_8O_{16} may absorb significant quantities of silver, barium and lead from aqueous solutions without loss of potassium, and it is probable that these ions enter the cryptomelane lattice in random positions. Whether this is so for $(NaMn)Mn_3O_7$ or whether the metals are exchanged for sodium as complex monovalent ions (*e. g.*, the ions $(ZnOH)^+$, $(ZnCl)^+$ suggested for the zinc montmorillonite clay complexes)[14] is a matter of conjecture.

Compounds resembling these "metal manganites" have previously been described. Gorgeu[15] prepared derivatives of a manganese oxide by boiling with solutions of metal acetates or sulfates. He found that the complexes contained 18% CuO, 19% ZnO, 21% MnO, 6.7% K_2O and also showed that iron, nickel, and cobalt deriva-

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[11] D. M. C. MacEwan, *Min. Mag.*, **28**, 36 (1947).

[12] J. S. Anderson, *Ann. Rep. Chem. Soc.*, **43**, 104 (1946

[13] J. W. Gruner, *Amer. Mineral.*, **28**, 496 (1943).

[14] M. M. Elgabaly and H. Jenny, *J. Phys. Chem.*, **47**, 399 (1943).

[15] A. Gorgeu, *Bull. soc. chim.*, [3] **4**, 16 (1890).

TABLE III

CRYSTALLOGRAPHIC DATA FOR HYDROUS MANGANESE OXIDE AND SOME DERIVATIVES

			Derivative		
		$(NaMn)Mn_3O_7$	Mn	Zn	Al
Cell dimensions, Å. (hexagonal)	a	8.41	8.41	8.41	8.59
	c	10.1	9.8	9.8	9.7
c/a		1.20	1.17	1.17	1.13
Cell contents		$Na_2Mn_{14}O_{28}\cdot 8H_2O$	$Mn_{16}O_{28}\cdot 8H_2O$	$Zn_2Mn_{14}O_{28}\cdot 8H_2O$	$Al_5Mn_{12}O_{28}\cdot 8H_2O$
Density, calcd.		3.77	4.04	4.10	3.86
Density, obs.		3.8	4.0	4.1	3.6

tives may be formed. The chemical similarity of these to the complexes of $(NaMn)Mn_3O_7$ is most striking. The oxidation of mixed solutions of manganous sulfate and various metallic salts with various oxidizing agents has also given rise to a series of "metal manganites."[16,17] Sarkar and Dhar[17] by this method prepared complexes of copper (13.5% CuO), lead (30.8% PbO), calcium (5.6% CaO), barium (17.5% BaO), aluminum (4.6% Al_2O_3) and other metals. The patterns of similar preparations were found by Feitknecht and Marti[4] to resemble that of manganous manganite. These authors believed the metal ions were held as intermediate layers in a double layer lattice, and that the formulas given by Sarkar and Dhar to represent their preparations were chance values of compounds of variable composition.

The derivatives of $(NaMn)Mn_3O_7$ may be given the approximate general formula $R_4O_7\cdot nH_2O$, where R represents the sum of the cations, and n lies between 1 and 2. The calcium derivative corresponds more nearly to $R_5O_9\cdot nH_2O$. They are not true compounds but may be regarded as metal derivatives formed in much the same way as the metal derivatives of zeolites, ultramarine and certain clay minerals are produced by a process of ion exchange. A distinction is the lack of reversibility. The relationship between some of these manganese oxide derivatives and certain naturally occurring minerals will be published in due course.[18]

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Summary

A hydrous manganese oxide of the approximate formula $(Na,Mn)Mn_3O_7\cdot nH_2O$ has been prepared by the oxidation of manganous hydroxide in aqueous alkaline suspension. From powder photographs it appears to have hexagonal symmetry, the sodium ions being loosely held between disordered structural units. On this assumption the unit cell has the dimensions $a = 8.41$, $c = 10.1$ Å.

The hydrous oxide readily forms metal complexes which, although resembling substances previously described, are not considered to be true compounds. The complexes are formed by the substitution of metal ions for sodium ions.

MELBOURNE, AUSTRALIA RECEIVED AUGUST 16, 1949

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[16] M. Salinger, *Z. anorg. Chem.*, **33**, 322 (1903).

[17] P. B. Sarkar and N. R. Dhar, *Z. anorg Chem.* **121**, 135 (1921).

[18] A. D. Wadsley, *Amer. Min.*, in press.