pared in good yields by the reactions of allylsodium and allylmagnesium bromide with optically active 2-bromoöctane. Samples of 3-methylnonane were prepared by the degradation of the optically active 4-methyl-1-decene and by synthesis from active 2-methyl-1-bromobutane. From a comparison of the rotations of these compounds, it was concluded that the allylmetallic condensations took place with inversion of configuration with less than 21% and more than 13% racemization.

Benzylmagnesium chloride reacted with (−)2-bromobutane to give a low yield of extensively racemized 1-phenyl-2-methylbutane.

EVANSTON, ILLINOIS RECEIVED MAY 18, 1949

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Systems of Boron Trifluoride with Phosphine, Arsine and Hydrogen Bromide

BY DONALD RAY MARTIN AND ROY EVERETT DIAL

Introduction

From the reviews of the coördination compounds of the boron halides by Booth[1] and Martin,[2,3] certain problems become apparent.

In Group 5a of the periodic classification, the following compounds of boron trifluoride with ammonia and phosphine have been reported: $NH_3 \cdot BF_3$, $(NH_3)_2 \cdot BF_3$, $(NH_3)_3 \cdot BF_3$, $PH_3 \cdot BF_3$ and $PH_3 \cdot (BF_3)_2$.[1] The existence of the last compound has been questioned by Wiberg and Heubaum.[4] It was decided to study the system boron trifluoride–phosphine inasmuch as there is no analogous compound formed by boron trifluoride with ammonia, nor by the other boron halides with phosphine (only $PH_3 \cdot BCl_3$, $PH_3 \cdot BBr_3$ and $PH_3 \cdot BI_3$? are reported[2]).

No compounds have been reported in which boron trifluoride is coördinated to an arsenic atom in any of its compounds, although $AsH_3 \cdot BCl_3$[2] and $AsH_3 \cdot BBr_3$[3] are known. Therefore, it was decided to investigate the system boron trifluoride–arsine.

Similarly, no compounds have been reported in which boron trifluoride is coördinated to a bromine atom in any of its compounds. Fluoboric acid is well known, but hydrogen chloride and boron trifluoride do not coördinate,[5] so it was of interest to see if this trend extended to hydrogen bromide. Therefore the system boron trifluoride–hydrogen bromide was investigated.

Experimental

Source of Reactants

Boron Trifluoride.—Gaseous boron trifluoride was obtained in a steel cylinder from the Harshaw Chemical Company, Cleveland, Ohio.

Arsine.—Sodium arsenide was prepared by fusing stoichiometric quantities of metallic sodium and metallic arsenic in a covered Hessian crucible. The reaction does not take place until the temperature is raised somewhat above the melting point of sodium. The reaction is very violent and lasts only for one or two seconds.

The apparatus used in the preparation of arsine consisted of a one-liter filter flask which served as a generator. A 250-ml. separatory funnel was attached to the generator with a one-hole rubber stopper. The side arm of the generator led to a safety manometer, and then in the order: a trap cooled with Dry Ice, a drying tube containing lumps of barium oxide, and a trap cooled with liquid air. A stopcock on the end of the last trap permitted the removal of any non-condensable gases present, the evacuation of the apparatus, or the withdrawal of the product. The Dry Ice-trap was used to remove most of the moisture from the generated gases and the barium oxide tube completed the desiccation. The product condensed in the liquid air trap.

The sodium arsenide was placed in the dry generator, and the apparatus was evacuated before any water was added to the generator through the separatory funnel. These precautions are necessary, because some free sodium may be present in the sodium arsenide. At least 30 ml. of liquid arsine was collected from 200 to 250 g. of sodium arsenide.

Phosphine.—The generating apparatus employed to prepare arsine was used also to synthesize phosphine. Crystalline phosphorous acid was placed in the generator and nitrogen added to the evacuated system until the pressure was 400 to 500 mm. Upon heating, the phosphine came off readily and smoothly. At lower pressures, the phosphorous acid failed to disproportionate and distilled into the Dry Ice-trap. About 40 ml. of liquid phosphine was obtained from about 400 g. of phosphorous acid.

A closed system, free of air, must be used for handling phosphine. The spontaneous combustion of phosphine in the apparatus does not harm the apparatus under low pressure, but leaves a reddish-orange deposit on the surface of the glass.

Hydrogen Bromide.—Hydrogen bromide was obtained in a steel cylinder from the Matheson Company, Joliet, Illinois.

Purification.—All gases used in the investigation were purified by fractional distillation as previously described.[6,7] They were stored in steel cylinders from which samples were withdrawn as needed.

Thermal Analyses.—The apparatus for establishing the mole fractions and to determine the freezing points of the various solutions was the same as previously described[5,8] except for the elimination of the use of polarized light in determining freezing points.

System: Boron Trifluoride–Phosphine.—The freezing point of the purified boron trifluoride used in this study was found to be −127.0 ± 0.3°. The purified phosphine was observed to freeze at −133.0 ± 0.3°. This value is

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[1] H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 4.

[2] D. R. Martin, *Chem. Revs.*, **34**, 461–473 (1944).

[3] D. R. Martin, *ibid.*, **42**, 581–599 (1948).

[4] E. Wiberg and U. Heubaum, *Z. anorg. Chem.*, **225**, 270–272 (1935).

[5] H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198–2205 (1942).

[6] D. R. Martin, *ibid.*, **67**, 1088 (1945).

[7] D. R. Martin and J. P. Faust, *J. Phys. Coll. Chem.*, **53**, 1255 (1949).

[8] H. S. Booth and D. R. Martin, *Chem. Revs.*, **33**, 57–88 (1943).

in good agreement with the value of −133.75° reported earlier.[9]

The data for this system are plotted in Fig. 1. Difficulty was encountered in getting all of the contents of the freezing point cell to melt. Therefore, the manometer on the freezing point cell was sealed off during the entire study and pressures of approximately 8 atmospheres were employed at times to attain the liquid state. When the mole per cent. of boron trifluoride exceeded 17.3, but was less than 84.1, the melting point of the solid was so high that the vapor pressure of the remaining liquid was in excess of 8 atmospheres. At these points the thermal analysis had to be discontinued.

The curve indicates the existence of two compounds whose melting points are approximately −48 and −83°. Two minimum points are known to exist; at 2 mole per cent. boron trifluoride and −145°, and at 98 mole per cent. boron trifluoride and −130°.

To complete the investigation of this system, it was decided to determine the molecular weights of a series of samples of the gases comprising the mixture in the cell until the cell was empty. The composition of any compounds present can be determined by this procedure. If the molecular weight is greater than those of either boron trifluoride or phosphine, then a stable compound exists in the gaseous state. On the other hand, if the molecular weight is between those of phosphine and boron trifluoride, the solid compound has dissociated to give a mixture of phosphine and boron trifluoride in the gaseous state. The ratio of phosphine to boron trifluoride can be calculated in either of these cases.

The molecular weights were determined by the Dumas procedure at 0°. The calibrated flask had a volume of 503.51 ml. Pressures were read to within 0.5 mm. using a Germann[10] manometer. Weighings were made on a large-size analytical balance to 0.01 g.

The first series of mean molecular weight determinations was made from a mixture of the two components containing an excess of boron trifluoride. The mean molecular weights are listed in Table I in chronological order.

TABLE I

Mol. wt. number	Wt., g.	Press., mm.	Mean mol. wt. of gas	Composition of gas
1	1.10	545.5	68.2	BF_3
2	1.08	540.5	67.5	BF_3
3	1.09	537.0	68.6	BF_3
4	1.03	538.0	64.7	$1PH_3:10BF_3$
5	1.00	562.0	60.1	$1PH_3:3.4BF_3$
6	0.50	300.5	56.3	$1PH_3:1.94BF_3$

After the gas for determination number 5 was withdrawn, the mixture in the freezing point cell looked as if all of the excess liquid boron trifluoride had been removed, leaving only a white, fluffy powder behind. The gas in the manifold was not recondensed into the cell. This procedure prevented contamination of the compound in the cell with any boron trifluoride in the manifold. Determination number 6 used the remainder of the material in the cell. The solid in the cell sublimed slowly as the temperature in the cell approached room temperature.

TABLE II

Mol. wt. number	Wt., g.	Press., mm.	Mean mol. wt. of gas	Compositior of gas
7	0.62	601.5	34.8	PH_3
8	.59	571.0	34.9	PH_3
9	.59	586.0	34.0	PH_3
10	.62	594.5	35.3	PH_3
11	.83	645.5	43.4	$1PH_3:0.38BF_3$
12	.23	151.0	51.5	$1PH_3:1.07BF_3$
13	.64	421.5	51.3	$1PH_3:1.05BF_3$

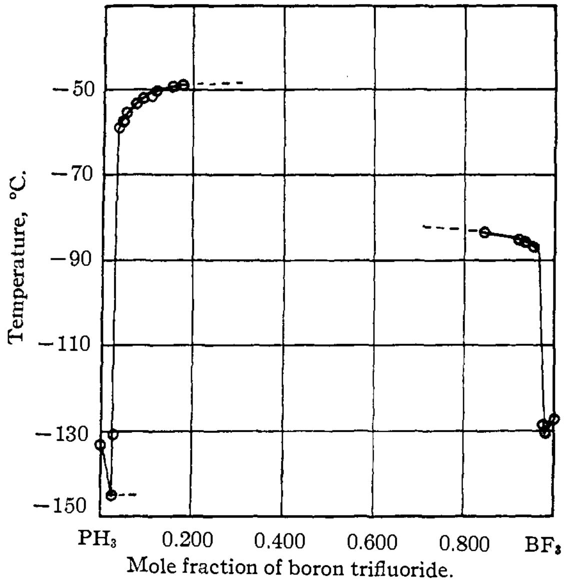

Fig. 1.—System boron trifluoride–phosphine.

The next series of mean molecular weight determinations was undertaken with an excess of phosphine. The results are listed in Table II.

In the above table the molecular weights of phosphine are consistently high, so the value of 51.5 for determination number 12 could easily be within the experimental error since the theoretical mean molecular weight of $PH_3 \cdot BF_3$ is 50.9.

After determination number 11, the gas in the manifold was not recondensed into the cell. Sample number 12 consisted of the gaseous products obtained from the remaining white solid.

Another mixture of boron trifluoride with an excess of phosphine was allowed to evaporate slowly until only a white powder remained in the cell. A molecular weight was determined using all of the white powder in the cell. The resulting mean molecular weight (number 13) agrees with determination number 12.

At this point it was felt that a series of molecular weight determinations should be made on a larger quantity of material so that more than one molecular weight of the molecular compounds could be obtained. These data are given in Table III.

TABLE III

Mol. wt. number	Wt., g.	Press., mm.	Mean mol. wt. of gas	Composition of gas
14	0.53	265.0	67.6	BF_3
15	.52	261.5	67.5	BF_3
16	.37	226.0	55.3	$1PH_3:1.70BF_3$
17	.40	268.5	50.4	$1PH_3:0.94BF_3$
18	.339	223.0	51.4	$1PH_3:1.07BF_3$
19	.094	61.0	52.0	$1PH_3:1.14BF_3$

After each of these determinations, the gas in the lines was not recondensed into the freezing point cell.

Evidence for the existence of $PH_3 \cdot (BF_3)_2$ was not obtained in this series of determinations. If the compound $PH_3 \cdot (BF_3)_2$ were present originally, it would be expected to decompose into $PH_3 \cdot BF_3$ and BF_3, because the second boron trifluoride molecule would not be held as strongly. Therefore, the solid left for the last 3 molecular weights

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(9) K. Clusius and K. Weigand, *Z. physik. Chem.*, **B46**, 1–37 (1940).

(10) A. F. O. Germann, THIS JOURNAL, **36**, 2456–2462 (1914).

should be $PH_3 \cdot BF_3$. Experiment number 6 in Table I would undoubtedly have given similar results had a sufficient quantity of the solid been available to fill the Dumas flask several times.

From Fig. 1 and the molecular weight studies, evidence is obtained for the existence of two coördination compounds between phosphine and boron trifluoride in the solid state, $PH_3 \cdot BF_3$ and $PH_3 \cdot (BF_3)_2$.

System: Boron Trifluoride–Arsine.—The temperature–composition diagram for this system is depicted in Fig. 2.

In this system the liquids, arsine and boron trifluoride, were observed to be immiscible in the region between 1.3 and 68.4 mole per cent. boron trifluoride.

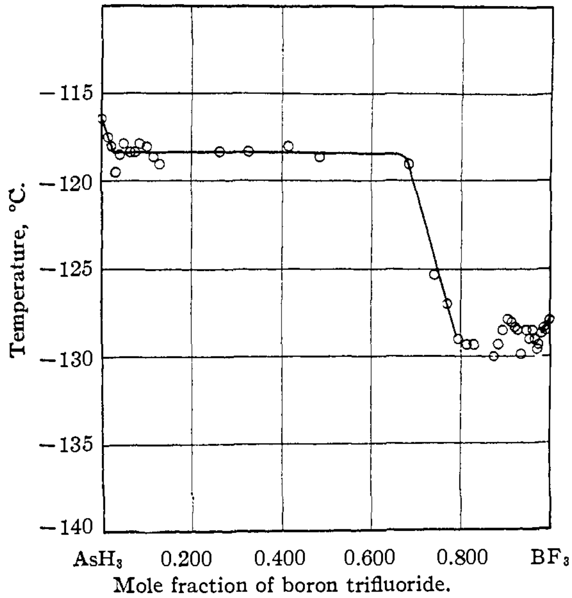

Fig. 2.—System boron trifluoride–arsine.

To study this system, a pressure as high as 4 atmospheres had to be employed at times. This permitted the contents in the cell to rise to a sufficiently high temperature to melt.

The freezing point of the purified arsine was observed to be −116.3 ± 0.3°, identical with the value in the literature.[11]

For compositions of 79 mole per cent. boron trifluoride and greater in Fig. 2, there was obtained a random distribution of points. Probably a simple eutectic point could be assumed for this portion of the curve, but the exact value for this point is difficult to establish. The curve is discontinued therefore between 79 and 96.3 mole per cent. boron trifluoride.

There is no evidence for the existence of a compound between arsine and boron trifluoride.

System: Boron Trifluoride–Hydrogen Bromide.—The data for this system are depicted in Fig. 3.

Immiscibility was encountered in the center of the diagram between 12.5 and 78.7 mole per cent. of boron trifluoride. These values give the limit of solubilities of each component in the other: 21.3 moles of hydrogen bromide in 78.7 moles of boron trifluoride and 12.5 moles of boron trifluoride in 87.5 moles of hydrogen bromide.

With less than 55 mole per cent. boron trifluoride the lower freezing points gave sharp, long breaks on the cooling curves, while the upper points produced very small breaks; and with more than 55 mole per cent. the upper freezing points were much more definite than the lower ones. The upper horizontal line in Fig. 3 denotes the temperature at which immiscibility in the liquid state first appears, while

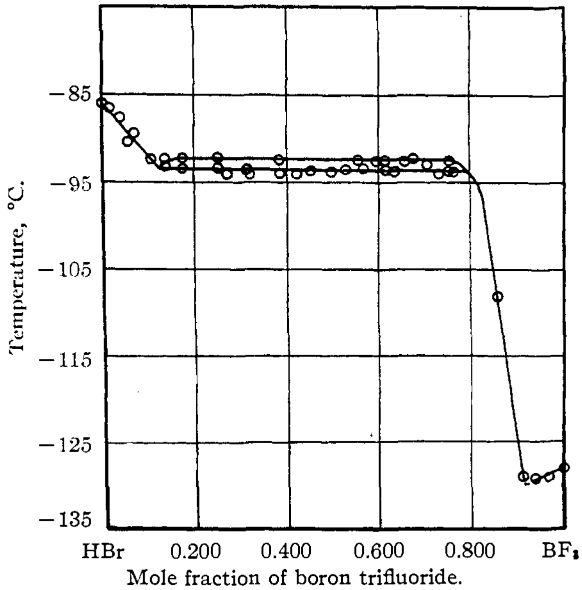

Fig. 3.—System boron trifluoride–hydrogen bromide.

the lower line indicates the temperature at which solid hydrogen bromide is crystallizing from solution.

The freezing point of the purified hydrogen bromide was observed to be −86.0 ± 0.3°. This value is a little higher than the value of −86.9° previously reported.[12]

It was necessary to employ pressures as great as 6 atmospheres in order to get some of the solid mixtures to melt.

No evidence was found for the existence of a compound between hydrogen bromide and boron trifluoride. A eutectic point was observed at −130.2° and 91.9 mole per cent. boron trifluoride.

Discussion

The phosphine–boron trifluoride system was expected to produce at least one compound and to settle the controversy with regard to the number of compounds formed between these two substances.

As previously pointed out, it might be expected that arsine would coördinate with boron trifluoride. However, in the analogy of the hydrides of Group 5a, the similarity of some properties of ammonia and phosphine does not continue to arsine. The reason for this change in properties between phosphine and arsine can possibly be explained by considering the electronegativities of the atoms involved. The nitrogen atom is more electronegative than hydrogen. This allows the nitrogen to pull the electron pairs of the hydrogen–nitrogen bonds closer to it, thus having control of enough electrons so that the "free pair" is capable of being shared with an acceptor atom.

The phosphorus and hydrogen atoms have about the same electronegativity, making it probable that the phosphorus atom still has its full share in five electrons, permitting the phosphorus to donate a portion of its unshared pair of electrons to an acceptor atom.

In arsine the hydrogen atoms are slightly more

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[11] W. C. Johnson and A. Pechukas, THIS JOURNAL, **59**, 2065–2068 (1937).

[12] W. F. Giauque and R. Wiebe, *ibid.*, **50**, 2193–2202 (1928).

negative than the arsenic atom. Therefore, the hydrogen atoms attract the electrons of the arsenic, leaving the arsenic atom with a slightly positive character, which may not allow the arsenic atom to be electrodotic.

Another approach in explaining why ammonia and phosphine form coördination compounds with boron trifluoride, while arsine does not, also accounts for the fact that arsine coördinates to boron trichloride and boron tribromide. It is postulated that steric hindrance due to the fluorine atoms in boron trifluoride prevents the arsenic atom of arsine from approaching sufficiently close to the boron atom to coördinate, even though the tendency for the arsenic and boron atoms to coördinate is probably great enough for a bond to be formed. In boron trichloride and boron tribromide there is less hindrance to the approach of arsine, and, even though the tendency to coördinate is less than with boron trifluoride, a bond can be formed.

Using the data in Table IV,[13] the approximate radii for the boron and halogen atoms in boron trifluoride and boron trichloride are calculated on the assumption that the sizes of the atoms in the respective molecules are linear functions of the ionic and covalent radii. The calculated values are given in Table V.

TABLE IV

Compound	BF_3	BCl_3
% Ionic character of bonds	63	22
Covalent radius of boron, Å.[a]	0.88	0.88
Ionic radius of boron, Å.	0.22	0.22
Covalent radius of halogen, Å.	0.64	0.99
Ionic radius of halogen, Å.	1.33	1.81

[a] The covalent and van der Waals radii of the arsenic atom are 1.20 and 2.00 Å., respectively.

TABLE V

Molecule	BF_3	BCl_3
Boron radii, Å.	0.48	0.67
Halide radii, Å.	1.07	1.17

When the boron trifluoride and boron trichloride molecules are drawn to scale, as in Fig. 4, using these radii, it is noted that there is less room for a large atom, like arsenic, to coördinate with the boron atom of boron trifluoride than with the boron atom of boron trichloride.

These calculated radii are not strictly correct. A rigid calculation is difficult to make, but the true radii are actually closer to the radii corresponding to the predominant character of the bond than are the calculated values of Table V. This means that in boron trifluoride the boron atoms should be *smaller* than 0.48 Å., and the fluorine atoms should be *larger* than 1.07 Å. Conversely, in boron trichloride the boron atom should be *larger*, and the chlorine *smaller*, than calculated. These modifications of the radii add to the steric hindrance in boron trifluoride, but allow more room for coördination to the boron atom in boron trichloride.

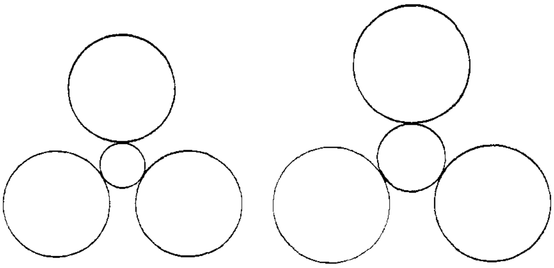

Fig. 4.—Boron halide molecules drawn to scale using radii in Table V: left, BF_3; right, BCl_3.

In addition, the larger chlorine atoms are more easily deformed than are fluorine atoms, as shown by the values of the bending and stretching constants in Table VI as determined by Yost.[14] The B–Cl bond can be stretched and bent, for small displacements, more than twice as easily as the B–F bond. The small bending and stretching constants for the B–Cl bond should allow the boron atom to be pulled out of the plane of the chlorine atoms into a pyramidal structure to a greater extent than in the case of boron trifluoride, exposing the boron atom to a greater extent.

TABLE VI

Compound studied	BF_3	BCl_3	BBr_3
Bending constant × 10^{-5}, dyne/cm.	0.88	0.43	0.27
Stretching constant × 10^{-5}, dyne/cm.	6.69	3.30	2.50
B–X bond distance, Å.	1.30	1.73	1.87

The results of the study of the system boron trifluoride–hydrogen bromide were expected in view of the behavior of hydrogen chloride with boron trifluoride.[5] Hydrogen fluoride forms a mono-, a di- and a trisolvate with boron trifluoride, whereas hydrogen chloride does not coördinate.[1,5]

Booth and Martin[5] believe that, in the coördination compounds of hydrogen fluoride with boron trifluoride, the donor is the fluoride ion, because in each of the above cases the hydrogen fluoride–boron trifluoride compounds were prepared in the presence of water.

It appears that the ionic character of the hydrogen to halogen bond may be a contributing, if not the controlling, factor in the formation of coördination compounds between the hydrogen halides and boron trifluoride. Hydrogen fluoride is 43% ionic,[15] whereas hydrogen chloride and bromide are only 17 and 11% ionic, respectively.[13]

Perhaps steric hindrance may prevent hydrogen bromide from coördinating with boron trifluoride, inasmuch as no bromine containing compound has been reported to coördinate to boron trifluoride. Neither has hydrogen bromide been reported to coördinate with the other boron halides.

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(13) L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1945.

(14) D. M. Yost, *Proc. Indian Acad. Sci.*, **8A**, 333-340 (1938).

(15) N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 171-173 (1946).

Summary

The systems phosphine–boron trifluoride, arsine–boron trifluoride and hydrogen bromide–boron trifluoride were investigated. Immiscibility of the liquid components was encountered in certain regions of the arsine–boron trifluoride and the hydrogen bromide–boron trifluoride systems. No evidence was found for compound formation between arsine and boron trifluoride, nor between hydrogen bromide and boron trifluoride. However, there is evidence that two coördination compounds exist between phosphine and boron trifluoride in the solid state, namely, $PH_3 \cdot BF_3$ and $PH_3 \cdot (BF_3)_2$.

It is postulated that the arsenic atom in arsine is too large to approach sufficiently close to the boron atom of boron trifluoride to coördinate, although the tendency for these atoms to coördinate is sufficiently great. It is calculated that less steric hindrance is encountered with boron trichloride than with boron trifluoride. This postulate explains the fact that arsine coördinates with boron tribromide and boron trichloride, but not with boron trifluoride.

It is believed that the ionic character of the hydrogen–halogen bond of the hydrogen halides is the controlling factor in the formation of coördination compounds between the hydrogen halides and boron trifluoride, accounting for the fact that the more ionic hydrogen fluoride forms three coördination compounds, whereas hydrogen chloride and hydrogen bromide form none.

URBANA, ILLINOIS RECEIVED APRIL 25, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Solid Oxides and Hydroxides of Manganese[1]

BY T. E. MOORE,[2] MARYLINN ELLIS AND P. W. SELWOOD

This paper describes an experimental study on the preparation and properties of the solid oxides and hydroxides of manganese. Special attention has been paid to the *identity* and *characterization* of each substance. The work was performed under contract with the Squier Signal Laboratory, Army Service Forces, Fort Monmouth, New Jersey, as part of their program for the improvement of dry cells.

Analytical and Experimental Methods

Analyses performed were for total manganese and for "active" oxygen. Manganese was determined by reaction with standard ferrous sulfate after all of the manganese had been oxidized to permanganate.[3] Solution of the sample was effected by treatment with dilute sulfuric acid containing ferrous sulfate. Oxidation of the manganese from a valence of two to seven was accomplished by the use of sodium bismuthate in nitric acid. This procedure was found satisfactory for all the preparations.

"Active" oxygen was determined by making use of the quantitative reaction of manganese in valence states greater than two with ferrous ion. A known excess of standard ferrous ammonium sulfate was employed in the dissolution of the sample and the excess was then titrated with standard permanganate.[4] The active oxygen content of the sample was then computed by multiplying the number of equivalents of ferrous ion oxidized by the manganese by the factor 8.00.

It should be pointed out that while these analytical methods proved satisfactory for our present purposes, they would not suffice without modification for the analysis of natural substances containing appreciable amounts of oxidizable elements such as iron.

All X-ray data reported here were obtained with powdered samples on a North American Philips Recording X-Ray Spectrometer. A copper target was used.

Magnetic susceptibility data were obtained on a Gouy balance, as described elsewhere.[5]

Preparative procedures are described under the individual compounds.

Manganese (Mon)Oxide

Preparation.—This compound occurs as the mineral *manganosite.* Classical methods for its synthesis include (a) reduction of a higher oxide, and (b) thermal decomposition of the carbonate or oxalate. The first method has been used by Millar[6] and others[7] in preparations for thermochemical studies. The second method has been the subject of a careful study by LeBlanc and Wehner.[8] This method was adopted for the work reported here, with minor modifications, as follows: J. T. Baker "reagent grade" manganous nitrate was recrystallized from water. The carbonate was precipitated by ammonium carbonate and washed free of ammonium and nitrate ions while protected from the air by a layer of

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[1] Presented in part at the Symposium on Galvanic Cells and Batteries at the Chicago meeting of the American Chemical Society, April 19, 1948.

[2] Present address: Department of Chemistry, Oklahoma A. and M. College, Stillwater, Okla.

[3] Blair, THIS JOURNAL, **26**, 793 (1904).

[4] Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 551.

[5] Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 2.

[6] Millar, THIS JOURNAL, **50**, 1875 (1928).

[7] Southard and Shomate, *ibid.*, **64**, 1770 (1942).

[8] LeBlanc and Wehner, *Z. physik. Chem.*, **A168**, 59 (1933).