present time. A number of the theories, offered to explain certain interesting cases of isomerism, were stated and illustrated by models showing the supposed special relations of the atoms contained in the compounds considered. The paper was attentively received and on motion the Section voted that it be published in the *Journal*.

Adjourned.

WM. C. DAY, *Secretary*.

A NEW PROCESS FOR THE MANUFACTURE OF MANGANESE ON THE COMMERCIAL SCALE.

BY WM. H. GREENE AND WM. H. WAHL.

[*Read at the stated meeting of the Chemical Section, held January 17, 1893.*]

Within a few years manganese has assumed considerable importance as a constituent of several alloys, and the purest manganese of commerce as well as the richest ferro-manganese have been unsatisfactory for the preparation of these alloys by reason of the high proportion of carbon invariably present.

About two years ago we were induced to undertake the search of a process for the manufacture on a commercial scale of metallic manganese that would contain a minimum of detrimental impurities and be absolutely free from carbon. Before describing the process which we have elaborated, we will review briefly the history of the element.

About 1774, Scheele and Bergmann demonstrated that the metallic radical of manganese dioxide is different from iron, and John* isolated the new element by heating a mixture of manganese carbonate and oil, powdering the resulting mass, again mixing it with oil and strongly heating in a brasqued crucible.

St. Claire Deville† modified this process as follows: He reduced pure artificially prepared dioxide to red oxide; mixed this with sugar charcoal in insufficient quantity to reduce the entire quantity of oxide, and heated the mixture in a lime crucible to the highest temperature of a wind furnace.

* *Gehlen's Jour. Chem. Phys.*, **3**, 452.

† *Ann. de Chimie et de Physique* [3], **46**, 182.

Brunner* heated manganese fluoride, or a mixture of manganese chloride and calcium fluoride, with sodium in clay crucibles.

Giles† prepared a manganese amalgam by the action of sodium amalgam on a concentrated solution of manganese chloride, and expelled the mercury by heating in a current of hydrogen, thereby obtaining pulverulent manganese.

Bunsen‡ obtained deposits of metallic manganese by electrolyzing a concentrated solution of manganous chloride.

The first attempt to produce the metal in considerable quantity appears to have been made by Hugo Tamm§ who in 1872 published the results of experiments made on certain modification of John's method. Native dioxide was reduced by heating with powdered charcoal and oil in the presence of silicious and fluorspar fluxes in graphite crucibles.

The problem presented to us was the reduction of a native oxide of manganese, for it is apparent that the expense of preparation of halogen compounds of the metal and their subsequent reduction would preclude the possibility of applying such a method to manufacturing on a commercial scale.

At the outset of our work it became evident that the first step in the process would be the purification of the ore from iron, which would inevitably be reduced in the reduction of the manganese and could not then be removed from the metal. Magnetic separation appeared to be the cheapest and most effective method, and we made exhaustive experiments in this direction, the ore being treated in all states of division and in all conditions of oxidation, between that of the natural ore and that in which the manganese was reduced to manganese monoxide and the iron to metallic iron. We were compelled to abandon the method entirely, because the iron and manganese are so intimately associated

* *Pogg. Annalen*, **101**, 264.

† *Philosoph. Mag.* [4], **24**, 328.

‡ *Pogg. Annalen*, **91**, 619.

§ *Chem. News*, 1872, 111.

in the ore that no satisfactory separation can be accomplished by the magnet.

We then tried various electro-chemical methods, the ore being made the anode of baths containing sodium chloride solution, ferrous sulphate, dilute sulphuric acid, etc. By such means a certain proportion of the iron may be removed, but the separation is slow, and is far from complete when the manganese oxides begin to be attacked.

Convinced that only a chemical method would answer the purpose, we found after a number of experiments that nearly all the iron can be removed from rich manganese ores by digesting the pulverized ore with about thirty per cent. sulphuric acid near the boiling point, while the manganese is practically unattacked. As an illustration of the effectiveness of the process, we may state that in a few hours the percentage of iron may thus be reduced from five or six to a few tenths, with a loss of not more than one per cent. of the manganese present. The copperas that may be obtained by treatment of the waste acid with scrap iron, will pay the cost of purification of the ore.

The reduction of the ore has been a perplexing problem. While it has never been denied that reduction by carbon in any form yields a metal containing a considerable proportion of the reducing agent, the literature of the subject indicated that this combined carbon might be removed by fusion of the metal under a layer of manganous carbonate or manganous oxide. Thus, Tamm* claims to have obtained, from a pyrolusite containing 79.5 per cent. Mn. and 6.5 per cent. F_2O_3 , a metal containing

Mn.	96.90
Fe	1.05
C	0.95
Other elements	1.10

and by refining this with manganese carbonate to have raised the proportion of manganese to 99.91 per cent. Other investigators admit the presence of more carbon in the product, but still claim that it may be removed by treatment

* *Chem. News*, 1872, 111.

with manganese carbonate. Our experiments show that the reduction by carbon takes place readily, and only after frequently repeated experiments, in which the proportions of oxide and carbon and the character and proportions of flux employed were varied through wide ranges, did we come to the conclusion that it is impossible by this method to prepare a metal containing less than about six per cent. of carbon, and that it is equally impossible by fusion with an oxidizing agent to remove carbon thus combined with manganese. The results of experiments recently published by Guntz* explain clearly these phenomena. He finds that carbon monoxide is rapidly decomposed by manganese at a red heat, carbon and manganese monoxide being formed. It can then be readily understood why carbon free manganese cannot be made in the electrical furnaces nor in graphite crucibles.

From all these facts we have been led to infer that the reduction of manganous oxide by carbon yields not manganese, but a definite carbide having the composition Mn_3C . We propose investigating this point in the future.

It then became evident that the problem could only be solved by a reduction taking place in the entire absence of carbon. Tentative experiments having given no encouragement to hope that an electrolytic method depending on the decomposition of fused baths of manganese chloride or manganese fluorides mixed with other chlorides and fluorides could be devised, the only alternative became a purely chemical process, the details of which were worked out during the progress of the laboratory work. The importance of these details will become apparent as we describe the steps of our process.

The pulverized manganese ore purified from iron, or containing less than one per cent. iron, is exposed to the action of reducing gases at a temperature approximating redness. All the manganese is thus converted into greenish-grey manganese monoxide, which must be allowed to cool out of contact with air to prevent oxidation to red manganoso-manganic oxide.

* *Comptes Rendus*, **114**, 115.

The monoxide is then mixed with about eighteen per cent. of its weight of granulated aluminum and a suitable flux and the mixture is heated to a temperature near the melting point of cast iron in magnesite crucibles. The flux may be silicious or a mixture of lime and fluorides, or lime alone. As soon as the temperature of reaction is attained the mass promptly fuses and must be poured from the crucible while at its maximum temperature. While the character of the flux has little influence on the reaction, it has important relation to the yield and quality of the metal obtained. A silicious flux naturally occasions the introduction into the manganese of a certain proportion of silicon. If the flux be too fusible a quantity of the aluminum may rise to the surface and escape the reaction. A mixture of lime and fluorspar has given us the best results in crucible operations.

Theoretically, one part of aluminum should yield three parts of manganese; the best results we have obtained on the small scale, producing several pounds of manganese at one operation have given us two and eight-tenths parts or ninety-three per cent. of the theoretical yield, and our average yield has been about eighty-seven per cent. With aluminum at its present price we therefore estimate that the absolute cost of producing carbon-free manganese containing, Mn ninety-six to ninety-seven per cent., Fe and Si each one to two per cent., by our process, will be within thirty-five cents a pound, this estimate including all expenses.

On the large scale we purpose conducting the operation on a magnesite lined hearth, reducing gases being in slight excess. By this means we believe that the manganese will be retained in the state of lowest oxide until the temperature of reaction is reached, and that the prompt fusion of the flux at this stage will protect the manganese formed from contamination by carbon from the flame.

We may mention in conclusion that having experienced considerable difficulty in obtaining and preparing magnesite crucibles, we adopted the expedient of lining plumbago crucibles with a stiff paste of calcined magnesite. When properly prepared, these linings do not crack on drying,

and do not shrink from the plumbago walls. After thorough drying, the crucibles are ready for use, and we have found the linings very serviceable, not only for the preparation of manganese, but in other metallurgical work in which silicious or plumbago crucibles were from any cause objectionable.

SOME PRINCIPLES THAT MUST BE OBSERVED IN ORDER TO MAKE A GOOD CLOSED-CIRCUIT BATTERY, AND A NEW PORTABLE DRY CELL DESCRIBED IN WHICH THESE PRINCIPLES ARE APPLIED.

BY E. F. NORTHRUP.

[*A paper read before the Electrical Section, Dec. 28, 1892; Jan. 24, 1893.*]

The different types of primary batteries now upon the market are very numerous. Those acquainted with the subject know that all are more or less defective and that few, if any, give the efficiency that the theory of galvanism would seem to promise. Much excellent and exhaustive work has been done in determining the laws of electrolytic action and the general principles of chemical electricity, but fewer persons with the requisite chemical and mechanical knowledge have devoted themselves to the actual construction of cells which shall be free from practical defects and closely realize the theoretical possibilities.

The following general considerations may help to indicate the necessary limits to improvements in batteries and the paths in which to make an advance.

Prof. F. B. Crocker has shown, in a paper published in vol. v of the *Proceedings of the American Institute of Electrical Engineers*, the necessary cost of electric energy obtained by chemical means, and has reached the conclusion that primary batteries can never approach the dynamo in respect to economy or efficiency. There are, however, numerous cases, such as bell work, telephone, telegraph, medical and testing work where the cost of electric energy