ON THE PREPARATION OF COLLOIDAL MANGANESE DIOXIDE

BY EUSTACE J. CUY

Three methods have this far been employed for the preparation of colloidal manganese dioxide.

I. The reduction of potassium permanganate. Marck\(^1\) used hydrogen peroxide as the reducing agent; Spring and de Boeck\(^2\) sodium thiosulphate; and Deisz\(^3\) arsenious acid. Frémy\(^4\) obtained a red solution of manganese dioxide, by treating potassium permanganate with concentrated sulphuric acid. He could not determine, however, whether he was dealing with a true or a colloidal solution.

II. The oxidation of manganous salts. Van Bemmelen\(^5\) used chlorine as the oxidizing agent. Trillat,\(^6\) using protective colloids such as albumin, gelatine, gum arabic, dextrose, etc., claims to have prepared colloidal manganese dioxide merely by exposing to the air alkaline solutions of manganous salts. He adduces, however, no conclusive evidence to prove that he was not dealing with complex organic salts such as complex copper glycerate C\(_4\)H\(_8\)(OH)\(_2\).O.Cu.O.C\(_2\)H\(_5\)(OH)\(_2\), complex copper tartrate Na — COO.CH — CH — COO.Na.

III. Advantage is taken of the fact that MnO\(_2\) is a reversible colloid. By carefully washing freshly precipitated manganese dioxide with conductivity water, Gorgeu,\(^7\) and also Spring and de Boeck\(^2\) were able to obtain colloidal solutions.

Of course, of the three methods, the last is the most difficult, since colloidal manganese dioxide is readily coagulated by salts. In the colloidal solutions as prepared by the other two methods there are present besides the MnO\(_2\) and the KOH formed during the reduction of the KMnO\(_4\) (which, however, has no appreciable coagulating effect since colloidal MnO\(_2\) is negatively changed) other substances, as for example, Na\(_2\)SO\(_3\), As\(_2\)O\(_5\), and in Trillat’s experiments, other colloids.
It seemed to us, therefore, worth while to make a brief summary of a new method of preparing colloidal MnO₂, which we developed while carrying out another investigation.

Potassium permanganate is a powerful but relatively slow oxidizing agent. For example, it does not oxidize Sørensen's salt \( \text{Na}_2\text{C}_2\text{O}_4 \) at ordinary temperatures, while it oxidizes completely at about 70° C. Similarly, potassium permanganate does not react at a measurable rate with \( \text{NH}_4\text{OH} \) at ordinary temperatures. If, however, to a hot concentrated \( \text{KMnO}_4 \) solution \( \text{NH}_4\text{OH} \) is added, \( \text{NH}_3 \) is oxidized to nitrogen and MnO₂ precipitates. If to a fairly dilute solution of \( \text{KMnO}_4 \), concentrated \( \text{NH}_4\text{OH} \) is added slowly, MnO₂ does not precipitate but remains in the colloidal form. After trying various concentrations of \( \text{KMnO}_4 \) and of \( \text{NH}_4\text{OH} \) we obtained best results by the following method:

Heat a \( M/100 \) permanganate solution to boiling. Then, while stirring, add concentrated \( \text{NH}_4\text{OH} \) one drop every 3 or 4 minutes. At no time should anything but the faintest smell of ammonia be perceptible. The solution should be kept at about 90° C. The solution gradually turns wine-red and finally coffee-brown by transmitted light and of a bluish brown oily color by reflected light. To test if all the permanganate has been reduced, a little of the colloidal solution can be coagulated by the addition of salt to show the presence of any violet color which might have been masked by the MnO₂. The intermediate red color may perhaps be due to the red form of MnO₂ which Frémy observed.

This reaction may possibly be made available as a qualitative or quantitative means of determining ammonia and ammonium salts. As will be seen from the equation \( 2\text{KMnO}_4 + 2\text{NH}_3 \rightarrow \text{N}_2 + 2\text{MnO}_2 + 2\text{KOH} \) or \( 2\text{MnO}_4^- + 2\text{NH}_4^+ \rightarrow \text{N}_2 + 2\text{MnO}_2 + 4\text{H}_2\text{O} \) in the final colloid there is present beside the MnO₂ only some KOH which, however, has a very small, if any, coagulating effect. This method eliminates the necessity of removing the electrolyte by dialysis, especially since, as Marck has found the colloid is coagulated by coming in contact with filter paper or parchment, so it cannot be dialyzed unless very special precautions are taken.
Preparation of Colloidal Manganese Dioxide

This colloid at all concentrations catalyses the decomposition of \( \text{H}_2\text{O}_2 \). The concentrated solutions are coagulated during the reaction while dilute solutions are unaffected.

We also found that varying amounts of this colloidal solution may be added to alcohol or alcohol added to the solution so that the ratio of \( \text{H}_2\text{O} \) to alcohol may vary all the way from zero to infinity without coagulating the colloid.

BIBLIOGRAPHY

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Chemical Laboratory
University of California
Berkeley