At 0° for certain concentrations of hydrogen peroxide the value $\frac{H_2O_2 \text{ in water}}{H_2O_2 \text{ in quinoline}}$ may be as low as 0.276.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

THE OXIDATION OF MANGANESE SOLUTIONS IN PRESENCE OF THE AIR.

BY VICTOR LENHER.

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It is well known that manganous solutions when neutralized undergo hydrolysis, and that when such solutions are allowed to stand in contact with the air, oxidation takes place with the precipitation of hydrated manganese dioxide. In the presence of the common alkalies, manganous salts yield manganous hydroxide, which when exposed to the air undergoes oxidation with the formation of hydrated manganese dioxide.

The deposition of pyrolusite, the most plentiful of the manganese ores in nature, is doubtless the result of a series of reactions of neutralization and oxidation. Manganese is presumably transported in nature as bicarbonate, sulfate, or chloride. When a manganese-bearing solution comes in contact with such a substance as calcium carbonate which is so widely distributed in nature, the manganese salt is neutralized, hydrolysis takes place, the action of the oxygen of the air steps in and manganese dioxide is precipitated, the calcium carbonate serving to neutralize the free acid which is liberated in the reaction.

In studying the reactions incident to the deposition of manganese dioxide by the neutralization of manganese salts and the subsequent oxidation by means of air, a series of observations have been made by the writer which at first sight seemed to be examples of certain principles of positive and negative catalysis.

A large number of glass tubes were cleansed with the utmost care and in each tube was placed a 1% solution of pure manganous chloride, a piece of Iceland spar, and a piece of metal, mineral or metallic compound. The solution and solids filled about one-fourth of the tube; the remainder of the space was occupied by air. These tubes were then sealed and allowed to stand for a long time in order to allow the slow oxidation by the air to take place. Very striking differences in behavior are exhibited by the various metals under these conditions. Certain of the metals cause the production of manganese dioxide to be accelerated, while others cause its formation to be retarded, or in some cases to be actually inhibited. Lead and bismuth accelerate the deposition of manganese dioxide from a manganese chloride solution when calcite is present as a neutralizing agent.

In blank experiments made with only manganese chloride solution and Iceland spar, the first noticeable separation of manganese dioxide appears only after standing for several weeks. With metallic lead present in the solution, a greater amount of the dioxide separates out overnight than in several weeks in the blank experiments. Certain other metals, such as tin, arsenic and antimony, prevent this oxidation of the manganese with formation of manganese dioxide. In fact they inhibit it entirely.

Such metals as mercury, copper, zinc, nickel, cobalt, cadmium, silver, gold, as well as mercuric sulfide, millerite, pyrite, chalcopyrite, and zinc blende, are without any effect in this reaction, the tubes at the end of a number of months of action appearing to be identical with those in which only the manganese solution and Iceland spar were present.

The acceleration of the oxidation of the manganese by the oxidation with air in presence of lead is not necessarily dependent on the presence of the metal itself, since lead sulfide, carbonate or sulfate also accelerate this reaction; nor is the reaction dependent on the use of the chloride of manganese, inasmuch as the sulfate or acetate of manganese also works equally well.

The retardation of this oxidation in the presence of metallic antimony, arsenic or tin, is readily explained by the reducing action of their salts toward manganese dioxide. The alkaline stannites, arsenites and antimonites reduce manganese dioxide; consequently in their presence it cannot be produced. The lack of reaction cannot, therefore, be regarded in the light of a negative catalysis.

Further, the presence of a higher oxide or salt of a higher oxide of these elements is without any appreciable effect on the reaction. Thus, in the presence of an arsenate, stannic oxide, or antimonic oxide, the oxidation and subsequent deposition of manganese dioxide proceeds in the same way as though these substances were absent.

The presence of a reducing substance when a neutralized solution of manganese is exposed to the air, impedes the oxidation and formation of manganese dioxide, or actually prevents it. Such substances which in general are not reducing in character, as the common metals mercury copper, cadmium, zinc, cobalt, silver, and the minerals cinnabar, millerite, pyrite, chalcopyrite, sphalerite, magnetite, hematite, corundum, bauxite and ilmenite, are without apparent influence on this oxidation.

Lead and lead compounds accelerate this oxidation greatly; bismuth and bismuth compounds also accelerate the oxidation, but to a lesser degree than lead.

From our numerous experiments along these lines, it is apparent that in the laboratory lead and lead compounds act as a great accelerator in the production of manganese dioxide when we attempt to imitate the agencies which apparently go on in nature in the formation of manganese deposits.

Thus far, however, no regular association of lead with the oxidized manganese minerals has been noted in the field, so far as the writer is aware.

MADISON, WIS.

[FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY.]

THE USE OF HYDROFLUORIC ACID IN THE SEPARATION OF SOME HEAVY METALS FROM TIN, ANTIMONY, TUNGSTEN, AND MOLYBDENUM, BY MEANS OF THE ELECTRIC CURRENT.

BY LEROY W. McCAY AND N. HOWELL FURMAN.

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About a year ago one of us (M.) showed that from a nitrohydrofluoric acid solution of copper, lead, tin, and antimony, the last two metals being in the higher state of oxidation, the electric current precipitates the copper and lead only, the former at the cathode, the latter as the peroxide at the anode.[1] It was stated then that, under similar conditions, silver and mercury can be separated from tin and antimony. Considerable experimental work has convinced us that the separation of silver and mercury from tin and antimony is as complete and their subsequent determination as exact as was observed in the case of copper and lead. The silver deposits contain no weighable amounts of platinum, which fact we attribute to the very weak currents necessarily employed in order to obtain compact silver deposits. The mercury deposits, however, usually contain a little platinum, as had already been noted in the case of copper deposited from nitrohydrofluoric acid solutions.[2] The amount found is variable, but seems to increase with the quantities of tin and hydrofluoric acid present, and with the time during which the current acts. When the current strength was as high as 3 A., and a Classen rotating anode was employed, the amount of platinum found in the mercury deposits was about 0.0005 g.; in one case 0.0007 g. On treating the deposits with nitric acid the platinum remains in the form of a black powder, or dark and very thin film, and can be rapidly and accurately determined, and the necessary correction made.

Since nitrohydrofluoric acid solutions of tungstic and molybdic acids behave toward the current like those of stannic and antimonic acids, copper, lead, silver and mercury can be separated from tungstic and molybdic as well as from mixtures of stannic, antimonic, tungstic and molybdic acids. The results for silver, copper and mercury are very satisfactory.

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[1] THIS JOURNAL, 36, 2375 (1914).

[2] *Loc. cit.*