POTASSIUM PERCARBONATE.

BY WILLIAM D. BROWN.

Received May 29, 1905.

SINCE Constam and Van Hansen described the method for the manufacture of potassium percarbonate,[1] it has been thought that it would be useful as an oxidizing agent. In the preparation of this compound the method of the above authors was followed rather closely.

Potassium percarbonate is prepared by electrolyzing a saturated solution of the carbonate at a temperature below 0° C. A porous cell of 200 cc. capacity was placed in a cylindrical vessel of such size that the outer or anode space had a capacity of 150 cc. In the porous cell was the cathode of nickel gauze and the cathode solution of 20–40 per cent. potassium carbonate. Around the porous cell, in the concentrated solution of potassium carbonate, a platinum wire was wound as a spiral. The whole was immersed in a mixture of ice and common salt, which brought the temperature down to —15° C.

A concentrated solution of pure potassium carbonate, at 15° C., has a specific gravity of 1.556. On lowering the temperature of this solution no crystallization takes place, but if the salt be impure, if a small quantity of common salt get into the solution, crystallization takes place on lowering the temperature, and, on passing a current, no crystals of potassium percarbonate are formed.

In reactions of this class it is necessary to have a high anode density and low cathode density. This was attained by having the nickel gauze cathode and platinum wire anode. The wire was 0.0345 cm. thick and 48 cm. long, making an anode surface of 0.05 sq. dm. The authors referred to state that an anode density of 60 amperes per sq. dm. should be used. Accordingly, a current of 3 amperes (and about 10 volts) was used. This heated the solution too much, and a mass of bicarbonate was formed. On shortening the wire to 24 cm., and passing a current of 1½ amperes (the density remaining the same) a mass of blue crystals was obtained floating in the anode solution. These were filtered by suction, when the blue color almost entirely disappeared.

Potassium percarbonate in solution behaves like hydrogen

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[1] *Z. Elektrochem.*, **3**, 445 (1897).

peroxide. A solution of percarbonate and an alkaline solution of hydrogen peroxide rapidly decompose, and at the same rate, while an acid solution of either does not lose strength on standing open. Moreover, an acid solution of percarbonate bleaches potassium permanganate. The reaction is $5K_2C_2O_6 + 8H_2SO_4 + 2KMnO_4 = 2MnSO_4 + 6K_2SO_4 + 8H_2O + 10CO_2 + 5O_2$. Accordingly, the strength of potassium percarbonate as an oxidizing agent was determined by titrating with permanganate in sulphuric acid solution. By titrating an aliquot part of the solution with hydrochloric acid (using methyl orange), the amount of potassium is obtained, and by comparing these the percentage of percarbonate in a mixture of percarbonate and bicarbonate is found. The product obtained in several experiments contained only from 30-40 per cent. percarbonate, while the authors mentioned state that a product of 80-95 per cent. percarbonate is obtained.

The formation of potassium percarbonate at this temperature, concentration, and anode density is attributed to the separation of K_2CO_3 into K and KCO_3, the KCO_3 uniting with another KCO_3 to form $K_2C_2O_6$.

A half pound of potassium percarbonate was received from Eimer and Amend. It had been rebottled by them from an importation of 10 pounds. The strength of this salt falls far below the normal. Dissolved in water and aliquot parts titrated with hydrochloric acid and permanganate, it showed a strength of 39.5 per cent. percarbonate. The salt is relatively stable, when kept in the dry state. Exposed over sodium hydroxide solution in a desiccator for twenty-four hours, 5 grams lost strength from 39.5 to 13 per cent. In the open air the strength fell in the same time to 21 per cent. In a large bell jar, connected with the air outside by a calcium chloride tube, the strength fell to 35 per cent. It also lost strength at the same rate when powdered and tightly corked in a small vial. The lumps in which it is purchased lose strength less rapidly than when powdered. Also the sample corked lost strength less rapidly than the sample from which we were using.

The similarity of the reactions of the solution of percarbonate and of the solution of hydrogen peroxide has been mentioned. The oxidizing reactions were studied further, a comparison being made with those of sodium peroxide. With a solution of chromium sulphate, sodium peroxide acts quicker than the percarbonate. But the greatest difference is shown in the case of their action on manganese sulphate; the peroxide throws down the brown precipitate of manganese dioxide, while percarbonate produces a small quantity of brown precipitate but mostly the light precipitate of manganese carbonate. On addition of sodium hydroxide to this precipitate in suspension, the dioxide is immediately formed. With a lead salt the same reactions occur.

From these reactions it would appear that the carbonate is formed, and this is oxidized slowly by the available oxygen contained in the solution as hydrogen peroxide. These salts were taken as perhaps the hardest to oxidize. The percarbonate readily oxidizes compounds such as ferrous and stannous salts. It will also liberate iodine from hydriodic acid solution.

Ordinarily, as an oxidizing agent sodium peroxide is to be preferred to potassium percarbonate. Moreover, the molecular weights are to be taken into account. The same amount of available oxygen is furnished by two and one-half times the amount of percarbonate as of peroxide.

In conclusion, potassium percarbonate can be produced from the pure carbonate, and is an oxidizing agent, but an oxidation reaction that cannot be caused by sodium peroxide remains to be found.

PITTSBURG, PA.

VOLUMETRIC METHODS FOR COPPER.

BY G. FERNEKES AND A. A. KOCH.

Received July 9, 1905.

IN LOOKING over the various volumetric methods for the determination of copper we found that a comparative study of the volumetric methods for this element had never been systematically taken up. We therefore decided to work over the principal methods for the purpose of ascertaining their scientific as well as their practical value. In each method the quantity of copper was varied, and the effect of interfering elements tried.

Carefully calibrated pipettes, measuring flasks and burettes were used. The copper sulphate for these experiments was prepared by C. A. F. Kahlbaum and was marked chemically pure. It, however, contained a trace of iron. With this copper sulphate several liters were prepared, so that 50 cc. contained approxi-