[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE PREPARATION OF HYDROGEN PEROXIDE

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In the course of work now in progress at this Laboratory, it became necessary to prepare, in moderate quantity, hydrogen peroxide free from inhibitors. We describe a simple method for obtaining 20% hydrogen peroxide directly and concentrating it to 90% with small loss. The method used in preparing 20% peroxide is a modification of one patented by Merck.[2]

Experimental Part

Sodium peroxide, C. P., was added in small portions with constant stirring to 20% sulfuric acid contained in a large beaker set in an ice-bath. The sodium peroxide was added slowly (the temperature of the solution never rose above 20°) until an amount equivalent to 95% of the sulfuric acid had been introduced. After standing for an hour the crystals of sodium sulfate decahydrate were filtered off and the filtrate was distilled in a vacuum at 60–65°. Since it was found by experiment that the hydrogen peroxide adhering to the crystals was sometimes as much as 20% of the whole, the crystals were thoroughly washed with cold water and the washings were added to the original filtrate. The solution was admitted to the distilling flask in 100cc. portions, a portion being added from a separatory funnel whenever the sodium sulfate in the distilling flask appeared dry. When the entire solution had been distilled, the temperature was raised to 85° to drive over any hydrogen peroxide combined with the sodium sulfate. The distillate was collected in two receiving flasks, the second of which was cooled to a lower temperature than the first. In the first flask there condensed a concentrated solution of hydrogen peroxide (over 20%); in the second, a dilute (less than 3%). No use was made of the dilute peroxide. In order to remove the small amount of chloride always present in the distillate, an excess of silver sulfate was added to the concentrated peroxide and the turbid liquid was distilled in a vacuum.

TABLE I

PREPARATION OF HYDROGEN PEROXIDE

Expt.	Na_2O_2, g.	Concd. soln., % of H_2O_2	H_2O_2 in concd. soln., g.	Dil. soln., % of H_2O_2	H_2O_2 in dil. soln., g.	Total yield, %	Yield of concd. H_2O_2, %
1	228	23.2	73.8	2.08	20.8	96	78
2	223	20.0	71.3	2.60	22.1	96	76

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[1] DuPont Fellow in Chemistry.

[2] Merck, Ger. pat. 152,173 (1903). See also Wagner's, *Jahresber. Chem. Tech.*, [1] **50**, 395 (1904).

Table I gives the yields of concentrated and of dilute hydrogen peroxide for two experiments.

After distillation from silver sulfate, the concentrated peroxide of Expt. 1 was 24.7%, and contained 69.1 g. of hydrogen peroxide. The loss in distillation was, therefore, 4.7 g., or 6.4%.

Table II shows the losses incurred, and the time required in concentration of the solution in Expt. 1 after removal of the chloride. The concentration was carried out in a vacuum desiccator over concd. sulfuric acid, at the temperature of the laboratory. The initial pressure in the desiccator was less than 1 cm. of mercury. All analyses were made by titration of a weighed sample with 0.1 *N* potassium permanganate solution.

TABLE II

CONCENTRATION OF HYDROGEN PEROXIDE

Days elapsed	Strength of H_2O_2, %	Solution, g.	Peroxide, g.	Loss, g.	Loss, %
0	24.7	280	69.1	..	..
1	38.8	170	65.9	3.2	4.6
2	52.6	122	64.1	5.0	7.3
2.3	69.7	89	62.0	7.1	10.3
3	88.0	63	55	13	19

Thus in three days 280 g. of 25% peroxide was concentrated to 63 g. of 88%, with a 19% loss. We did not attempt to concentrate the peroxide beyond this point, since Maass and Hatcher[3] have shown that the loss by volatilization from solutions containing more than 90% of peroxide is enormous.

Discussion

Vanino[4] describes the preparation of 20% solution of hydrogen peroxide by addition of sodium peroxide to sulfuric acid as not suitable for laboratory practice, and recommends the substitution of phosphoric acid for sulfuric; we found, however, that due to the foaming of the phosphoric acid solution during distillation sulfuric acid is to be preferred.

We found that an ordinary oil pump provides a satisfactory method of obtaining a vacuum during distillation. With a sulfuric acid trap between the receiving flasks and the pump, we did not notice any thickening of the oil as reported by Maass and Hatcher.

Wolfenstein[5] concentrated dilute solutions by evaporation at atmospheric pressure, but when the solution contained more than 45% of peroxide the loss by volatilization was large. By means of a sulfuric acid concentrator and pump, Maass and Hatcher concentrated solutions of hydrogen peroxide in a short time, with small loss. As a typical case, they reported

[3] Maass and Hatcher, THIS JOURNAL, **42,** 2548 (1920).

[4] Vanino, "Präparative Chemie," Enke, Stuttgart, 2nd. ed., **1921,** vol. 1, p. 10.

[5] Wolfenstein, *Ber.*, **27,** 3307 (1894).

that 528 g. of 24.3% peroxide was concentrated at 0° to 102 g. of 91.1% material. The yield was, therefore, 65%; the time taken was four hours. It is interesting to notice that in comparison Maass and Hatcher cite an experiment of Wolfenstein's, in which he concentrated 802 g. of 4.5% peroxide to 66.6% and obtained a 28.3% yield. This experiment was not carried out under reduced pressure, as they state, but was performed in an evaporating dish on a water-bath at 75°.

Summary

A quantitative study has been made of the preparation of concentrated solutions of hydrogen peroxide. A simple method of concentrating hydrogen peroxide solutions to 90% has been described. The yields obtained are excellent.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

MOLYBDENUM THIOCYANATE AND THE QUALITATIVE DETECTION OF MOLYBDENUM

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The red color produced by the action of reducing agents on a soluble hexavalent molybdenum compound in the presence of a thiocyanate salt in acid solution appears to have been first noticed by Braun[2] in 1867. Skey[3] also described it in the same year.

In 1903, Chilesotti[4] electrolyzed a solution containing hexavalent molybdenum, obtaining as a consequence a solution of molybdenum trichloride. This salt, combined in water solution with potassium or ammonium salts, produced a red solution presumably of the composition K_3MoCl_6.

He found later that this double salt added to potassium thiocyanate yielded on crystallization an orange-red double potassium molybdenum salt of the composition $K_3Mo(SCN)_6.4H_2O$.[5] According to Sand and Burger,[6] hexavalent molybdenum electrolytically reduced in the presence of ammonium thiocyanate gave thiocyanate salts of quadrivalent molybdenum. These salts were obtained with pyridine or quinoline of crystallization by extracting the water solution with ether and extracting this ether

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[1] This material is taken from the thesis of Mr. C. E. Swartz presented in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

[2] Braun, *Z. anal. Chem.*, **6**, 86 (1867).

[3] Skey, *Chem. News*, Am. Reprint I, 296 (1867).

[4] Chilesotti, *Atti. accad. Lincei*, **12**, ii, 22, 67 (1903).

[5] Chilesotti, *Gazz. chim. ital.*, **34**, ii, 493 (1904).

[6] Sand and Burger, *Ber.*, **38**, 3384 (1905).