density, its boiling point at 760 mm. and its vapor pressure at different temperatures up to its boiling point have been made. The boiling point was found to be 96.4° at 760 mm. and the density 1.1545 g./cc. at 20°. The vapor pressure conforms well to the equation $\log P_{\text{mm.}} = 7.7085 - (1782.8/T \text{ abs.})$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Oxyacids of Fluorine. II

BY L. M. DENNIS AND E. G. ROCHOW

In a "Communication to the Editor"[1] we briefly described experiments that seemed to indicate the formation of an oxyacid of fluorine when fluorine is passed into a solution of cesium carbonate or of the hydroxides of potassium, lithium or calcium, and also upon the passage of the gas into a suspension of calcium carbonate in water.

The research has been continued, and although it is as yet by no means completed, a brief report upon its progress is here given.

Fluorination of Aqueous Solutions.—Wartenberg and Klinkott state[2] that in their study of the reactions

$$2F_2 + 2NaOH \text{ (dilute)} = 2NaF + H_2O + F_2O$$
$$F_2O + 2NaOH \text{ (concentrated)} = 2NaF + H_2O + O_2$$

they found no evidence of the formation of a salt of an oxyacid of fluorine.

In their interesting investigations of oxidation with fluorine, Fichter and Bladergroen[3] passed fluorine into a cold, concentrated solution of potassium hydroxide and observed that the solution had oxidizing power, which they ascribed to the formation of potassium ozonate. Baeyer and Villiger, however, state[4] that potassium ozonate has no oxidizing action. Traube later found[5] that when solid potassium hydroxide is subjected to long treatment with ozone at about −12° and is then dissolved in ice-cold sulfuric acid and titrated with potassium permanganate, a fraction of 1% of hydrogen peroxide is present.

It seems reasonable to assume that the action of fluorine upon a cold solution of an alkali hydroxide is analogous to that of chlorine, and that the first stage of the reaction is

$$F_2 + 2NaOH = NaFO + NaF + H_2O$$

the unstable sodium hypofluorite then slowly breaking down with the liberation of F_2O

$$2NaFO + H_2O = 2NaOH + F_2O$$

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(1) THIS JOURNAL, **54**, 832 (1932).

(2) Wartenberg and Klinkott, *Z. anorg. allgem. Chem.*, **193**, 409 (1930).

(3) Fichter and Bladergroen, *Helv. Chim. Acta*, **10**, 549 (1927).

(4) Baeyer and Villiger, *Ber.*, **35**, 3038 (1902).

(5) Traube, *ibid.*, **45**, 2201 (1912).

To ascertain whether the oxidizing power of such a solution could be due to ozone (hydrogen peroxide) or whether an oxidizing compound of fluorine (hypofluorite?) is probably formed, the following experiments were made.

Ozone was passed for ten minutes through a 50% solution of potassium hydroxide cooled to −40°. The solution became deep yellow in color (potassium ozonate), the color persisting if the temperature was held at −30° or below. Samples of the solution at various temperatures were added to a solution of potassium iodide and sufficient sulfuric acid to render the resulting solution acid. The mixture was allowed to stand for three minutes, and was then titrated with sodium thiosulfate.

Similarly, a 50% solution of potassium hydroxide at −40° was treated with fluorine,[6] and samples taken at the same temperatures as before were titrated with sodium thiosulfate. The results were as shown.

Solution of Potassium Hydroxide Treated with

Ozone		Fluorine	
Sample taken at	I liberated by 1 g. of solution, mg.	Sample taken at	I liberated by 1 g. of solution, mg.
−20°	None	−20°	6.17
0°	0.0996	0°	4.63
18°	.0786	18°	3.02
After standing 53 hours at 20°	.0578	After standing 70 hours at 20°	0.279

The results for the oxidizing power of the fluorinated solution are of the same order as those obtained by Fichter and Bladergroen,[3] although the experimental conditions were quite different.

Another sample of a 50% solution of potassium hydroxide was cooled to −40° and was treated with fluorine for fifteen minutes. The solution was then evaporated to complete dryness in a beaker over a free flame and was fused in the beaker. When cold, the residue was dissolved in water and a portion, when acidified with sulfuric acid, liberated iodine from potassium iodide immediately and in considerable amount.

These results seem clearly to demonstrate that the oxidizing power of a solution of potassium hydroxide that has been treated with fluorine is not due either to ozone or hydrogen peroxide. Nor can the oxidation be due to fluorine monoxide, for that gas is quickly and completely decomposed by strong alkaline solutions.[7]

When aqueous solutions are fluorinated, a large part of the fluorine acts on the water alone, and in fluorination of solutions of basic hydroxides or carbonates, the small amount of the oxidizing product is mixed with very large amounts of the inorganic fluoride that is simultaneously produced. To avoid these drawbacks recourse was had to the

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(6) The cell that was used for the preparation of free fluorine was that devised by Dennis, Veeder and Rochow, THIS JOURNAL, **53**, 3263 (1931).

(7) Ruff and Menzel, *Z. anorg. allgem. Chem.*, **190**, 257 (1930).

Electrolysis of Molten Electrolytes

A preliminary experiment, in which a molten mixture of potassium hydroxide and potassium fluoride was electrolyzed in a silver crucible as cathode and a graphite rod as anode, gave a product that, upon solution in water and acidification with nitric acid, yielded a precipitate which contained silver and fluorine. Conversion of the substance to silver sulfate showed that it closely corresponded to $AgFO_3$.

The melting point of the electrolyte was then lowered by using a mixture of LiOH, NaOH, KOH, NaF and KHF_2. A large silver crucible was used as the cathode, and a smaller silver crucible having minute perforations in the bottom was employed as a diaphragm to decrease the cathodic reduction of the anodic oxidation product. A graphite rod was again used as anode. This procedure doubled the yield of the oxysalt of fluorine. The electrolysis was run for two hours with a current of 1.5 amp.

The contents of the crucible was dissolved in water, made slightly acid with nitric acid and silver nitrate was added. There resulted a white precipitate which was found to be only very slightly soluble in water, but readily soluble in ammonium hydroxide. It was washed with water, dissolved in ammonium hydroxide, and reprecipitated with nitric acid. Spectroscopic examination showed that fluorine was present.[8]

Examination of the precipitate under the microscope showed the presence of two types of crystals, one of which was identified as silver chloride[9] by its crystal form and its microchemical reactions. To ascertain the characteristics of the other type, a sample was mounted in a mixture of sulfur and selenium of a suitable refractive index[10] which rendered the silver chloride invisible and brought out distinctly the crystals of the other substance. These were found to be anisotropic, probably tetragonal or rhombic, and of lower refractive index than those of silver chloride.

Another sample of the crystalline precipitate was then subjected to x-ray examination by the powder method. The material showed the typical pattern of the cubic crystal of silver chloride, and in addition there appeared a series of weaker lines which were identified as those produced by a simple tetragonal lattice. The indices of the indicated crystal planes, and the lesser dimension of the unit cell calculated for each, were as follows.

Indices	110	002	200	121	003	203	101 (3)
a_0	5.33	5.32	5.32	5.26	5.34	5.35	5.40

The axial ratio of such a crystal is 1.14, and the calculated density is 3.37. The relationship of the substance to silver chlorate and silver bromate is shown by the following data.

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[8] Papish, Hoag and Snee, *Ind. Eng. Chem.*, *Anal. Ed.*, **2**, 263 (1930).

[9] The hydroxides used in the electrolysis contained small amounts of chlorides.

[10] Merwin and Larsen, *Am. J. Sci.*, 4th Series, **34**, 42 (1912).

$AgFO_3$(?)	$d = 3.37$ Tetragonal
$AgClO_3$	$d = 4.43$ Tetragonal
$AgBrO_3$	$d = 5.21$ Tetragonal

The above evidence is strongly indicative of the formation of silver fluorate.

The investigation is being continued.

Summary

The treatment of concentrated, cold solutions of fixed alkali hydroxides with fluorine forms a product of comparatively high oxidizing power, and evidence is presented to show that the oxidation cannot be due either to an alkali ozonate, ozone, hydrogen peroxide or fluorine monoxide. When a molten mixture of alkali hydroxides and fluorides is electrolyzed, there is formed an oxysalt of fluorine. Examination of the silver salt of this oxy-acid indicates that it is silver fluorate, $AgFO_3$.

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Notes

The Absorption Spectra of *m*-Bromophenol Indophenol, 2,6-Dibromophenol Indophenol and Guaiacol Indophenol

BY MATILDA MOLDENHAUER BROOKS

The absorption curves of *m*-bromophenol indophenol, 2,6-dibromophenol indophenol and guaiacol indophenol have been measured in 0.0001

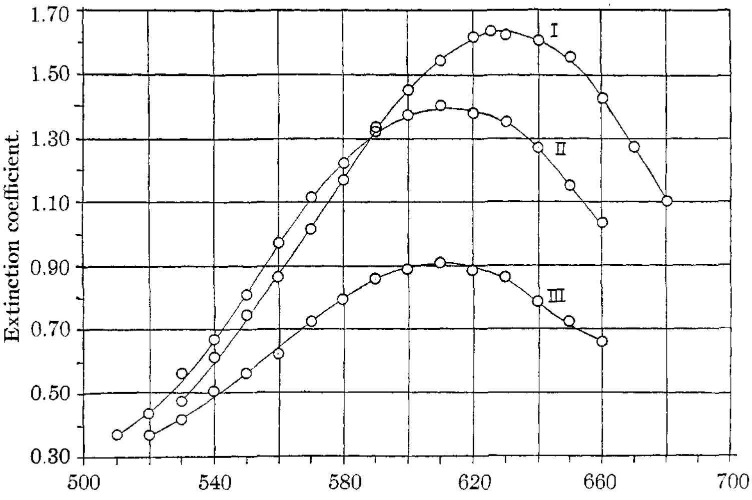

Fig. 1.—I, *m*-bromophenol indophenol; II, 2,6-dibromophenol indophenol: III, guaiacol indophenol.