

XXVIII.—*On a remarkable Salt deposited from the Mother-Liquors obtained in the Manufacture of Soda.*

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IN a paper recently read before the Glasgow Philosophical Society (*Chem. News*, vol. xxv, 55), Mr. Mactear, of the St. Rollox Chemical Works, drew attention to the formation of fine ruby-coloured octohedral crystals in the highly concentrated mother-liquors obtained in the manufacture of soda by Leblanc's process. The occurrence of these crystals has been already observed. Rammelsberg (*Jahresbericht. f. Chem.*, 1864, 185) found for them the composition  $\text{Na}_3\text{PO}_4 + 10\text{H}_2\text{O}$ , and attributed their colour to the presence of a small quantity of vanadic acid. Baumgarten (*Jahresbericht.*, 1865, 219) however, has shown that this salt has in reality a more complicated composition; it invariably contains fluorine, and must be regarded as a double salt of trisodium phosphate and sodium fluoride. It would stand, therefore, to trisodium phosphate in a relation similar to that in which fluorapatite stands to tricalcium phosphate.

Mr. Mactear kindly furnished me with some specimens of these crystals for analysis. They were unusually large, being several centimeters in diameter; although their edges were considerably abraded, the octohedral habitus of the crystals was perfectly distinct. On treating them with cold water, they left a small quantity (1.74 per cent.) of insoluble matter, consisting of sulphide (sulphur, 0.3 per cent.) and phosphate of iron, and the solution became blue, or greenish blue. This coloration disappeared on standing, and on filtration a colourless solution was obtained, from which by evaporation colourless and perfectly regular octahedrons were obtained. These crystals consisted essentially of trisodium phosphate, containing small quantities of fluorine and vanadic acid, and traces of arsenic acid and silica. On standing in contact with the air, the solution absorbed carbonic acid, and ordinary rhombic phosphate of sodium was deposited.

The octohedral crystals were analysed with the following results:—

1.8995 grm. lost at  $130^\circ$ , 0.8783 grm. water, = 46.2 per cent. On gentle ignition, 0.9230 grm., or 48.60 per cent. water was given off.

The residue on solution in water gave, after addition of silver nitrate, 2·265 grams of mixed phosphate and vanadate of silver.

The vanadic acid was estimated in the original substance by titrating with a dilute potassium permanganate solution. Two experiments were made. No. 1 gave 0·74 per cent.; No. 2, 0·71 per cent.  $\text{VO}_4$ . After removal of the excess of silver, the sodium was estimated as sulphate. Wt. of  $\text{Na}_2\text{SO}_4 = 1\cdot3195$ . These numbers agree perfectly with those required by the formula proposed by Baumgarten, viz.,  $2\text{Na}_3\text{PO}_4 + \text{NaF} + 19\text{H}_2\text{O}$ , as the following comparison shows:—

	Found.	Calculated.
Water.....	48·60	48·01
Phosphoric acid ( $\text{PO}_4$ )....	26·02	26·67
Vanadic acid .....	0·73	—
Arsenic acid .....	traces	—
Sodium .....	22·52	22·63
Fluorine .....	—	2·69
		100·00

Baumgarten attributes the red colour of the original crystals to sulphide of iron; the colouring matter, whatever it may be, is very irregularly distributed throughout the crystals.