47. *The Ternary System Potassium Permanganate–Potassium Fluoborate–Water.*

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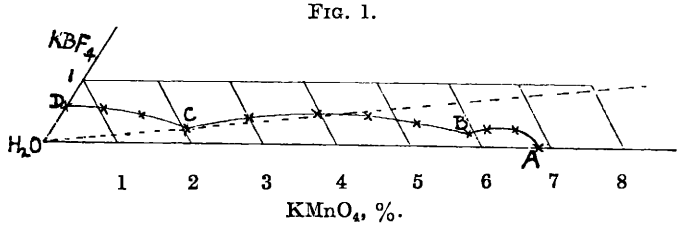
THE formation of a double salt between potassium fluoborate and potassium chlorate has been described by Zambonini (*Z. Kryst.*, 1905, **41**, 60) and Barker (J., 1912, **101**, 2484), but some doubt appears to exist whether potassium fluoborate forms a double salt

FIG. 1.



with potassium permanganate also. Zambonini (*Atti R. Accad. Lincei*, 1922, **31**, 67) has stated that there is a slight miscibility, up to 0·4% of potassium permanganate, with potassium fluoborate, but on the permanganate side the miscibility is practically zero. It was found, however, that when crystals of potassium fluoborate are suspended in a saturated solution of potassium permanganate, overgrowth crystals are formed. A phase-rule study of the system was therefore undertaken in order to determine whether double salts or only mixed crystals (solid solutions) of limited composition are formed.

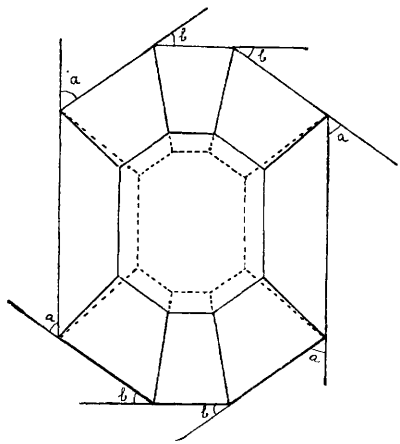
Pure samples of potassium fluoborate and potassium permanganate were obtained by recrystallisation, and mixtures of the two salts and water were made in various proportions in the usual manner. Equilibrium was obtained in 2 days in a thermostat at 25° ± 0·1°.

The composition of the solid phase was determined by the method of Schreinemakers (*Z. physikal. Chem.*, 1893, **11**, 81), as shown by the relevant corner of the triangular diagram in Fig. 1.

The permanganate in the solid and solution was estimated by titration against standard oxalic acid after suitable dilution of weighed portions, and the fluoborate by difference between this result and that obtained by evaporation to dryness of suitable portions. The total potassium was estimated as sulphate as a check. The results of analysis are given in Table I.

A double salt of the composition $KBF_4,6KMnO_4$, containing approximately 12% of fluoborate and 88% of permanganate, occurs as a solid phase between the limits 6·03—2·07% of potassium permanganate. Its saturation curve is concave towards the water vertex.

FIG. 2.



The *double salt* was prepared by crystallising a solution of 1 part of potassium fluoborate with 7·6 parts of potassium permanganate (Found: $KMnO_4$, 88·27. $KBF_4,6KMnO_4$ requires $KMnO_4$, 88·3%). Its crystals (see Fig. 2) are transparent and pink. They consist of eight-sided tablets, belong to the rhombic system (orthorhombic bipyramidal), and have axial ratios $a : b : c = 1·68 : 1 : 1·23$, which agree fairly well with those

TABLE I.

System KBF_4–$KMnO_4$–H_2O at 25°.

Point on Fig. 1.	Solutions. Percentages, by weight. KBF_4.	Solutions. Percentages, by weight. $KMnO_4$.	Wet solids. Percentages, by weight. KBF_4.	Wet solids. Percentages, by weight. $KMnO_4$.	Solid phase.
A	—	6·90	—	—	$KMnO_4$
	0·28	6·76	8·28	89·14	
	0·33	6·32	11·18	85·45	
B	0·22	6·03	12·22	84·85	$KMnO_4$; $KBF_4,6KMnO_4$
	0·37	5·42	11·48	85·18	$KBF_4,6KMnO_4$
	0·48	4·78	11·71	84·55	
	0·50	4·08	11·12	84·45	
	0·41	3·19	8·20	87·80	
C	0·22	2·07	16·25	81·87	KBF_4; $KBF_4,6KMnO_4$
	0·46	1·58	76·34	18·89	KBF_4
	0·54	1·12	88·72	8·93	
D	0·57	—	—	—	

measured for potassium fluoborate by Montemartini (*Gazzetta*, 1894, **24**, i, 478). The angle a is approximately 54°, and b is approximately 36°.

Summary.

The system KBF_4–$KMnO_4$–H_2O has been studied at 25°. The anhydrous double salt, $KBF_4,6KMnO_4$, has been isolated. It forms pink, tabular crystals somewhat of the same form as potassium fluoborate.

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