A NEW DOUBLE OXALATE OF BISMUTH AND POTASSIUM.

BY F. B. ALLAN AND J. S. DELURY. Received May 20, 1903.

By dissolving bismuth oxalate in concentrated, hot potassium oxalate and cooling the solution, Souchay and Lensson¹ obtained a substance to which they gave the formula

 $Bi_{2}(C_{2}O_{4})_{37}K_{2}C_{2}O_{4}24H_{2}O$

and from the mother-liquor they got a further deposit having the composition

$$Bi_2(C_2O_4)_3IIK_2C_2O_424H_2O.$$

Svensson² has also described a double salt having the composition

 ${\rm Bi}_{2}({\rm C}_{2}{\rm O}_{4})_{3}{\rm K}_{2}{\rm C}_{2}{\rm O}_{4}{\rm 2}{\rm H}_{2}{\rm O}.$

When a small quantity of bismuth oxalate is stirred with a saturated potassium oxalate solution, the solid phase is found to be potassium oxalate containing only a trace of bismuth, the bismuth oxalate having displaced the potassium oxalate in the solution. If more dilute solutions of potassium oxalate be used, the solid phase approaches the composition $\text{Bi}_2(\text{C}_2\text{O}_4)_3\text{K}_2\text{C}_2\text{O}_4$, but the double salt was not obtained pure in this way.

Bismuth oxalate was boiled with a 20 per cent. solution of potassium oxalate; the hot solution was filtered and, on cooling, deposited small, white crystals. These crystals, dried under pressure, were dissolved in hydrochloric acid and the solution, after the removal of bismuth, was evaporated to dryness, ignited, and the potassium determined as potassium chloride; the bismuth was determined as the sulphide and the oxalic acid by titration with permanganate.

Calculated for Bi ₂ (C ₂ O ₄ ¹ ₃ K ₂ C ₂ O ₄ .9½ H ₂ O.		Found.
Bismuth	40.94	40.91
C_2O_4	34.56	34.54
Potassium	7.69	7.69
Water	16.81	(16.86)

A 21 per cent. and a 23 per cent. solution of potassium oxalate gave the same double salt. Bismuth oxalate was then boiled with a solution of potassium oxalate saturated at room temperature, and the deposit at 50° contained 36.1 per cent. C_2O_4 while that ob-

² Ber. d. chem. Ges., 3, 314.

¹ Ann. Chem. (Liebig), 105, 245.

tained by cooling the same solution from 50° to room temperature contained 51.9 per cent. C_2O_4 . As the oxalates described by Souchay and Lensson would contain 41.9 per cent. and 49 per cent. C_2O_4 respectively, it seems probable that the precipitates from the more saturated solutions are mixtures of the double salt described above and potassium oxalate.

CHEMICAL LABORATORY UNIVERSITY OF TORONTO, May, 1903.

A NEW DOUBLE OXALATE OF BISMUTH AND AMMONIUM.

By F. B. ALLAN AND T. A. PHILLIPS. Received May 20, 1003.

SOUCHAY AND LENSSON¹ dissolved bismuth oxalate in concentrated, hot ammonium oxalate solution and obtained, on cooling, a double salt to which they gave the formula

 $Bi_2(C_2O_4)_39(NH_4)_2C_2O_424H_2O_1$

Their analyses do not agree very closely with that formula, and as some experiments made in this laboratory threw doubt on the existence of this complex double salt, their work has been repeated.

A 4 per cent. solution of ammonium oxalate was boiled with bismuth oxalate, using a reflux condenser, for about half an hour, and filtered hot. On cooling, this solution deposited small, white crystals which were dried, under pressure, between paper. The salt was easily soluble in hydrochloric acid. The bismuth was determined as the sulphide, the oxalic acid by titration with permanganate, and the ammonia distilled over by boiling with potash. absorbed in hydrochloric acid and determined in the usual way.

$\begin{array}{c} \text{Calc}\\ \text{Bi}_2(\text{C}_2\text{O}_4)_3(1)\end{array}$	ulated for NH ₄) ₂ C ₂ O ₄ 8H ₂ O.	Found.
Bismuth	43.93	44.30
C_2O_4	37.08	36.85
Ammonium	3.81	3.78
Water	15.18	(15.07)

Bismuth oxalate is only slightly soluble in ammonium oxalate, and large quantities of the solution must be used in preparing the double salt, so that imperfect filtering or the slight solubility of basic salt formed during the boiling would account for the high value found for bismuth and the corresponding low values for oxalic acid and ammonia.

¹ Ann. Chem. (Liebig), 105, 245.