

The *ammonium salt* of phenylcyanthiolmethylpseudothiurea was obtained when the pseudothiurea was heated at 100° for five hours with alcoholic ammonia saturated with hydrogen sulphide. On cooling, no pressure was found in the tube and, on concentrating the solution, colorless needles separated which, after two recrystallizations, melted at about 142°-143° to a pale yellow liquid. A nitrogen determination gave:

	Calculated for	Found.
	$C_6H_5N=C(-SCH_3)-NHCN.NH_3C_6H_{12}N_4S.$	
Nitrogen.....	26.82	26.79

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THE BASIC OXALATES OF BISMUTH.

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IN recent papers the author has given the results of researches on the nitrates¹ and sulphates² of bismuth, making use of the phase rule to determine the number of phases present, and thus to know whether the solid to be analyzed was one phase or a mixture of two phases. In a monovariant system of three components, we may have a gaseous, a liquid, and two solid phases. In a divariant system, only three phases can exist and there can be only one solid in addition to the liquid and gaseous phases, and it is only in the latter case that we can call the solid a chemical compound. In the experiments referred to, both monovariant and divariant systems were obtained, but as three weeks were sometimes necessary to obtain equilibrium in a monovariant system, no attempt has been made to get other than divariant systems in this research.

Heintz³ added oxalic acid to a solution of bismuth oxide in nitric acid, and boiled the precipitate repeatedly with water. He supposed that the neutral oxalate is first formed, and that it is decomposed by water; he gives the resulting substance the formula $Bi_2O_3 \cdot 2C_2O_3 \cdot 1\frac{1}{2}H_2O$. Schwartzenberg⁴ boiled bismuth oxide with acid potassium oxalate, and the product dried at 100° agreed with the formula $Bi_2O_3 \cdot 3C_2O_3 \cdot 4H_2O$. Souchay and Lensson⁵ prepared the neutral oxalate and gave the composition of the air-dried salt

¹ *Am. Chem. J.*, **28**, 307.

² *Ibid.*, **27**, 284.

³ *Pogg. Ann.*, **63**, 90.

⁴ *Ann. Chem. (Liebig)*, **64**, 127.

⁵ *Ibid.*, **105**, 245.

TABLE A.

Temp. 50°. $\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ } in $\text{Bi}_2\text{O}_3\cdot 3\text{C}_2\text{O}_3 = 2.15$.
 } in $\text{Bi}_2\text{O}_3\cdot 2\text{C}_2\text{O}_3 = 3.23$.

Components.		Time.	Composition of solution.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid.
1 gram neutral oxalate.	100 cc. water.	3 days	0.0225 N. oxalic acid.	3.33
2 grams " "	100 " "	3 "	0.0435 " "	3.27
3 " " "	100 " "	3 "	0.0647 " "	3.26
4 " " "	100 " "	3 "	0.0857 " "	3.25
2 " " "	100 cc. 0.042 N. oxalic acid.	7 "	0.085 " "	3.25
2 " " "	100 " 0.019 " "	3 "	0.069 " "	2.21
2 " " "	100 " 0.14 " "	3 "	0.138 " "	2.15
2 " " "	100 " 0.21 " "	3 "	0.205 " "	2.16
2 " " "	100 " 0.34 " "	3 "	0.34 " "	2.12
2 " " "	100 " 0.70 " "	3 "	0.68 " "	2.12

as $\text{Bi}_2\text{O}_3 \cdot 3\text{C}_2\text{O}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$, while Muir¹ gave it the formula $\text{Bi}_2\text{O}_3 \cdot 3\text{C}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. I could not obtain this salt free from the basic oxalate although it was stirred for several days with a concentrated oxalic acid solution. Souchay and Lensson boiled the neutral oxalate repeatedly with water and obtained the basic salt $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and Muir repeating this preparation gave it the formula $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3$.

In the following experiments, the neutral oxalate, containing some basic oxalate, was stirred with water or oxalic acid solutions, the apparatus used being the same as that previously described. The composition of the solid contents was determined by the analysis of the liquid phase.

TABLE B.
Temp. 75°.

Components.		Time.	Composition of solution.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid
1 gram neutral oxalate	100 cc. water			
1 gram neutral oxalate	100 cc. water	3 days	0.024 N. oxalic acid	3.35
2 grams " "	100 " "	3 "	0.046 " "	3.27
3 " " "	100 " "	3 "	0.068 " "	3.28
4 " " "	100 " "	3 "	0.090 " "	3.26
5 " " "	100 " "	3 "	0.122 " "	3.21
6 " " "	100 " "	3 "	0.135 " "	3.25

At 50° the basic salt is in equilibrium with oxalic acid solutions up to 0.085 normal, and at 75° up to at least 0.135 normal. In the sixth experiment in Table A the reaction is delayed by the initial strength of the oxalic acid solution. The basic salt obtained in these experiments was air-dried and dissolved in hydrochloric acid. The bismuth was determined as the sulphide and the oxalic acid in the filtrate was titrated directly with permanganate, as the small quantity of hydrochloric acid present did not effect the result.

	Calculated for $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$.	Found.
Bi_2O_3	74.16	74.14
C_2O_3	22.97	23.00
H_2O	2.87	(2.86)

Miller and Kenrick² have shown that the number of possible phases is not changed if a new constituent be added to the liquid phase, provided that this new constituent does not pass into the solid phase. This condition is fulfilled, if dilute ammonia is stirred with $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and therefore a divariant system

¹ *J. Chem. Soc.* (London), 1878, p. 193.

² *Trans. Roy. Soc., Canada*, 1901.

TABLE C.
Temp. 75°.

Components.				Time.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid.
1 gram $\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$,	100 cc. 18	per cent. NH_4NO_3	and 0.0275 N. NH_3	1 day	3.55
I " "	100 " 18	" "	" 0.0457 "	I "	3.84
I " "	100 " 18	" "	" 0.01 "	I "	5.28
I " "	100 " 3.6	" $(\text{NH}_4)_2\text{C}_2\text{O}_4$	" 0.0275 "	I "	3.20
I " "	100 " 3.6	" "	" 0.0457 "	I "	3.20
I " "	100 " 3.6	" "	" 0.091 "	I "	3.20

TABLE D.

Temp. 75°. $\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in $3\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 = 9.69$.

Components.						Time.	Composition of solution.		$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid.
I gram	$\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$.	100 cc.	0.028 N	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	and 0.0462 N. NH_3 .		2 days	0.0703 N. oxalate (neutral).	
I	"	100	"	0.028	"	"	0.0578	"	8.82
I	"	100	"	0.028	"	"	0.0693	"	9.70
I	"	100	"	0.028	"	"	0.0809	"	9.70
I	"	100	"	0.028	"	"	0.0925	"	9.79
I	"	100	"	0.028	"	"	0.104	"	9.90
I	"	100	"	0.028	"	"	0.115	"	9.70
I	"	100	"	0.028	"	"	0.138	"	10.50

still contains but one solid phase. In the following experiments, ammonia of varying strength was used and another basic salt was obtained. Preliminary experiments showed that the new basic salt was acted upon by quite dilute ammonia, and in order to obtain this solid phase in equilibrium with a larger range of concentrations of ammonia, it was necessary to reduce the efficiency of the ammonia in the reaction. This can be done by adding to the solution any ammonium salt, thus decreasing the amount of ionization, and as ammonium oxalate is one of the products of the reaction, it is the best salt for this purpose. Table C contains a comparison of the rate of reaction in the presence of ammonium nitrate and of ammonium oxalate, and shows that although the ammonium oxalate was more dilute, the reaction was much quicker in the ammonium nitrate solution.

Nos. 2 to 7 in Table D are divariant systems with one solid phase. The solid contents of these bottles were filtered off, air-dried, and analyzed.

	Calculated for $3\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3$.	Found.
Bi_2O_3	90.64	90.42
C_2O_3	9.36	9.47

This basic salt has not been previously described.

TABLE E.
Temp. 50° .

Components.		Time.	$\frac{\text{Bi}_2\text{O}_3}{\text{C}_2\text{O}_3}$ in solid.
1 gram	$\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3$	100 cc. 0.093 N. NH_3	4 days 1.16
I	"	100 " 0.465 "	4 " 2.21
I	"	100 " 0.07 N. KOH	4 " 6.63
I	"	100 " 0.10 "	4 " Bi_2O_3 .

Table E shows the results obtained when the higher basic oxalate reacts with more concentrated ammonia, or with potassium hydroxide. There is no indication of another basic salt.

Neutral bismuth oxalate was stirred with solutions of potassium oxalate and of ammonium oxalate, but the reaction was found to be slow, and it was difficult to obtain equilibrium. The composition of the solids obtained indicated the existence of double salts having the formulas $\text{Bi}_2(\text{C}_2\text{O}_4)_3(\text{NH}_4)_2\text{C}_2\text{O}_4$ and $\text{Bi}_2(\text{C}_2\text{O}_4)_3\text{K}_2\text{C}_2\text{O}_4$, and Souchay and Lençon's experiments in which they found more complex double salts were repeated, and the products analyzed by Messrs. DeLury and Phillips. Their results are published in this Journal.