

**PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF THIOSULPHATES
OF METALS—PART V**

**THERMOMETRIC STUDIES OF BISMUTH THIOSULPHATE
COMPLEXES**

by

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The composition of bismuth thiosulphate has been studied by the method of thermometric titrations between bismuthnitrate and sodium thiosulphate in aqueous and alcoholic medium. The direct titration curve suggests the formation of $\text{Na}_3\text{Bi}(\text{S}_2\text{O}_3)_3$ in which the ratio of Bi : S_2O_3 is 1 : 3. In the reverse titrations also the formation of $\text{Na}_3\text{Bi}(\text{S}_2\text{O}_3)_3$ is indicated.

There is meagre amount of literature on the study of the composition of bismuth thiosulphate. A. Carnot and O. Hausers¹ suggested the formula $\text{R}_3\text{Bi}(\text{S}_2\text{O}_3)_3 \cdot n\text{H}_2\text{O}$ and he pointed out that the solutions of these salts contain $\text{Bi}(\text{S}_2\text{O}_3)_3$ complex anion which break up readily. There is however hardly any reference in literature to the study of bismuth thiosulphate by physico-chemical methods. Hence the present investigation by applying thermometric method was considered worthwhile.

In view of the difficulties associated with analytical work and to throw further light on the composition of bismuth thiosulphate, attempts have been made in this paper to study the composition of these complexes by thermometric method. With the results of potentiometric, conductometric and amperometric measurements in progress, the results of thermometric method have been incorporated and discussed in this paper.

Experimental

The reagents used were of E. Merck, quality, Standard solutions were prepared by weighing. In case of sodium thiosulphate few drops of chloroform were added during the preparation of the solution so that the solution may be serviceable for a longer time. The strength of the hypo solution was further checked by standard KIO_3 solutions². Bismuth nitrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was prepared by direct weighing and the solution was estimated as bismuth oxy-iodide.³

The arrangement for thermometric titrations was the same as has been described by Haldar⁴. Using different concentrations of the two salts in solution, the titrations were followed by the direct and reverse methods (i.e., when $\text{Bi}(\text{NO}_3)_3$ was added from burette to sodium, thiosulphate solution in thermos flask and *vice versa*).

Titration were also carried out in presence of alcohol upto 20% by volume. The total rise in temperature was then plotted against the titre in c.c.

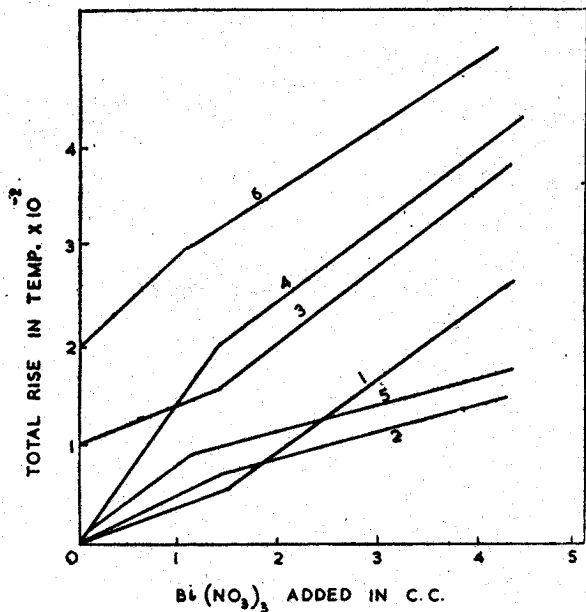
Summary of thermometric Observations

Table No.	Fig. No.	Curve No.	Bi(NO ₃) ₃ conc.	Hypo-conc.	Points showing breaks Formula				Ratio
					Med.	Calc.	Obsd.	Supported	
DIRECT TITRATION									
1	1	1	M/5	M/20 20 c.c	Aq.	1.66	1.6	Na ₃ Bi (S ₂ O ₃) ₃	1 : 3
2	1	2	"	18	Alc 10%	1.50	1.5	"	"
3	1	3	"	16	20%	1.33	1.4	"	"
4	1	4	M/5	M/25 20	Aq.	1.33	1.4	"	"
5	1	5	"	18	Alc. 10%	1.20	1.2	"	"
6	1	6	"	16	20%	1.06	1.1	"	"
REVERSE TITRATIONS									
7	2	1	M/80 20 c.c	M/5	Aq.	3.75	3.7	Na ₃ Bi (S ₂ O ₃) ₃	3 : 1
8	2	2	18	"	Alc 10%	3.375	3.4	"	"
9	2	3	16	"	20%	3.00	3.9	"	"
10	2	4	M/125 20 c.c	M/10	Aq.	4.8	4.8	"	"
11	2	5	18	"	Alc. 10%	4.32	4.30	"	"
12	2	6	16	"	20%	3.84	3.80	"	"

Discussion

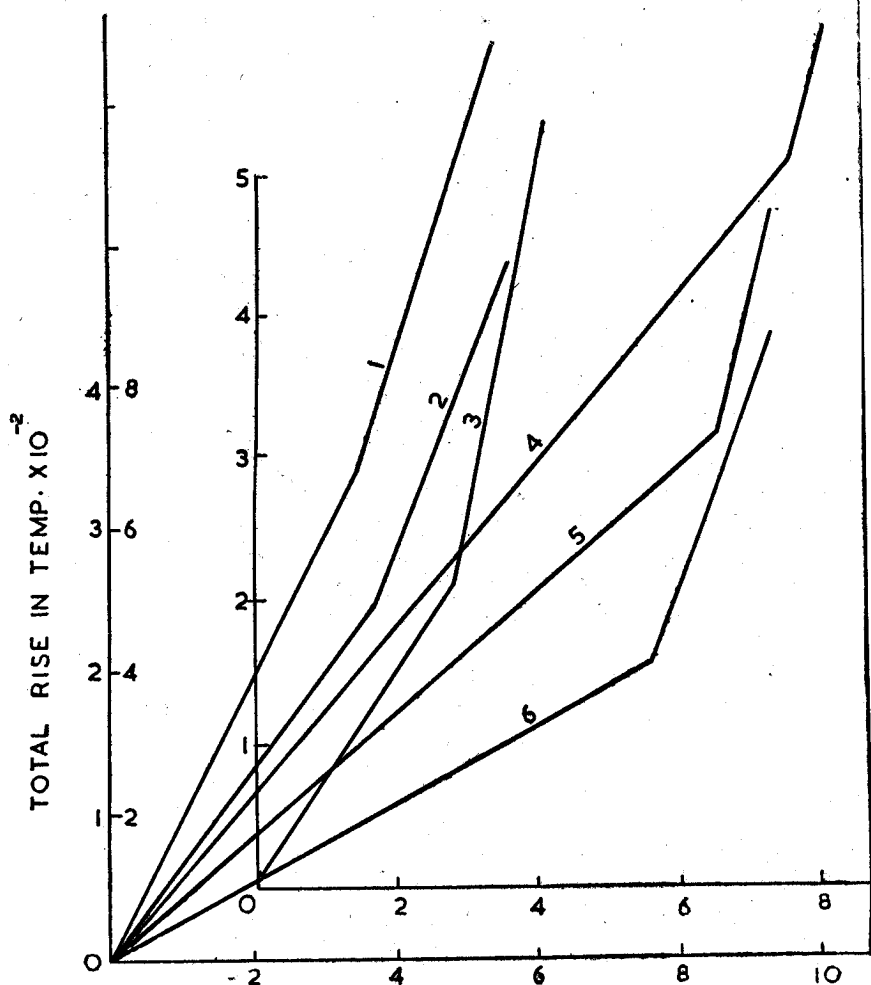
It is evident from the summary of the observations of thermometric titrations that in the direct titrations the theoretical titre values required for the formation of Na₃Bi (S₂O₃)₃ would be (table 1 to 6) 5.0, 4.5, 4.0, 2.0, 1.8 and 1.6 respectively in the ratio of 1 : 3. In the direct titrations one break occurs at the point of equivalence in the ratio 1 : 3. The theoretical values, calculated for the reverse titrations accordingly for the ratio 1 : 1 are (tables 7 to 12) 1.25, 1.125, 1.00, 1.6, 1.44 and 1.28 respectively and therefore theoretical titre value required for the ratio 3 : 1 would be 3.75, 3.375, 3.00, 4.80, 4.32 and 3.84 respectively. The observed values in the reverse titrations are in agreement with the titre values for ratio 3 : 1. Thus the formation of the same compound Na₃Bi (S₂O₃)₃ is supported.

With a view to show the discrepancy between the observed and calculated titre values, a summary of observations in aqueous and alcoholic solutions is given above for comparison.



The results of our thermometric method are accurate and fairly support the views of O. Hauser⁵.

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References

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