333. *The System* $Na_2S_2O_3$–$Ag_2S_2O_3$–H_2O *at* 25°.

By HENRY BASSETT and JOHN T. LEMON.

THE sodium silver thiosulphates are of interest in connexion with the photographic fixing process, but there is a difficulty in obtaining them pure. A discussion of the results of earlier work is given by Baines (J., 1929, 2763). Most investigators agree in reporting two double salts: (*a*) $Na_4Ag_2(S_2O_3)_3,2H_2O$, readily soluble and crystallising in clusters of lustrous platelets; (*b*) $NaAgS_2O_3,H_2O$, sparingly soluble and crystallising in small hard pointed crystals. Baines, in common with other recent investigators, corrected the first to $Na_5Ag_3(S_2O_3)_4,2H_2O$, and also definitely established the existence of $NaAgS_2O_3,H_2O$, for which he gave crystallographic data.

Results of the Present Investigation.—The following four salts have been found capable of stable existence in contact with solutions of suitable composition at 25°: (1) $Na_3Ag(S_2O_3)_2,2H_2O$ or $3Na_2S_2O_3,Ag_2S_2O_3,4H_2O$, readily soluble in water, microscopic platelets of rhombs often with the acute angles truncated; (2) $Na_5Ag_3(S_2O_3)_4,2H_2O$ or $5Na_2S_2O_3,3Ag_2S_2O_3,4H_2O$, readily soluble, microscopic needles; (3) $NaAg(S_2O_3),H_2O$ or $Na_2S_2O_3,Ag_2S_2O_3,2H_2O$, sparingly soluble, pointed granular crystals, readily observed by the naked eye; (4) $NaAg_3(S_2O_3)_2,H_2O$ or $Na_2S_2O_3,3Ag_2S_2O_3,2H_2O$, very slightly soluble, microscopic square or rectangular platelets which often have two opposite corners truncated.

The apparent absence of any phenomena of metastability in this system, and the behaviour noted during the microscopic observation of the action of water on the salt (4) render it unlikely that any salts, other than those described, can exist in stable or metastable equilibrium at 25°.

All the salts are colourless, non-congruent, and are comparatively stable in contact with mother-liquor with the exception of (4).

Discussion of Results.—Of the above four double salts, the first three have previously been reported by earlier investigators.

(1) $Na_3Ag(S_2O_3)_2,2H_2O$ was obtained by Spacu and Murgulescu (*Z. anorg. Chem.*, 1932, **208**, 157), who also reported the formation of $Na_4Ag_2(S_2O_3)_3,2H_2O$, anhydrous $NaAgS_2O_3$, and $Na_2Ag_4(S_2O_3)_3,4H_2O$, for none of which we could obtain any evidence. From its description as lustrous platelets, leaflets, etc., it seems not unlikely that the salt $Na_4Ag_2(S_2O_3)_3,2H_2O$ reported by many earlier investigators consisted of $Na_3Ag(S_2O_3)_2,2H_2O$ contaminated with some $Na_5Ag_3(S_2O_3)_4,2H_2O$.

(2) $Na_5Ag_3(S_2O_3)_4,2H_2O$ had been definitely established by Baines (*loc. cit.*) and has been reported by Rosenheim and Trewendt as a trihydrate (*Ber.*, 1928, **61**, 1731).

(3) $NaAg(S_2O_3),H_2O$ is the most definitely established, and was obtained by nearly all earlier workers. Its degree of hydration has been settled by Baines (*loc. cit.*) and confirmed in the present work.

(4) *Sodium trisilver thiosulphate monohydrate* has not previously been reported. It has an extremely small range of existence, for it is only formed within 1% of the H_2O

point of the triangular diagram. It is the only one of the sodium silver thiosulphates to have an Ag/Na atomic ratio greater than 1/1; it is produced by the action of water, or more particularly of dilute (N/10) silver nitrate, on $NaAgS_2O_3,H_2O$.

Increasing insolubility and decomposition rendered it impossible to continue the solubility curve beyond the point for $NaAg_3(S_2O_3)_2,H_2O$.

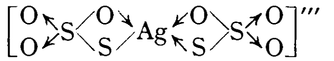
Silver thiosulphate, $Ag_2S_2O_3$, has only been obtained in the form of an unstable, insoluble, amorphous, white precipitate, and, probably owing to its instability, its analysis has never been reported. In contact with solution it gradually decomposes, the decomposition being greatly accelerated by the presence of excess of silver ions (Herschel, *Edin. Phil. J.*, 1819, **1**, 8, 396; 1820, **2**, 154; Fogh, *Compt. rend.*, 1890, **110**, 709; Müller, *Z. anorg. Chem.*, 1924, **134**, 202).

Reported Isomerism of Sodium Silver Thiosulphates.—Colourless and yellow sodium silver thiosulphates were reported by Meyer and Eggeling (*Ber.*, 1907, **40**, 1351). They were supposed to be isomerides, silver being attached to oxygen in the one case, and to sulphur in the other. Nothing of the kind was observed in the present investigation, and Jonsson (*Ber.*, 1921, **54**, 2556) found that the case was probably not one of isomerism since reaction with ethyl iodide indicated that the silver atom was attached to sulphur in both cases. The confusion is probably due to decomposition, since conversion of the colourless salt into the yellow isomeride was commonly effected by cautiously warming it with water.

Colourless and yellow sodium cuprous thiosulphates undoubtedly exist, but are not isomeric.

Nature of the Complex Salts.—It would appear that the complex ammonium, potassium, rubidium, or cæsium silver thiosulphates are nearly all anhydrous (Rosenheim and Steinhäuser, *Z. anorg. Chem.*, 1900, **25**, 72; Meyer and Eggeling; Jonsson; Rosenheim and Trewendt, *locc. cit.*). This makes it probable that the water molecules in the sodium analogues are attached to this ion—probably as $[Na_2(H_2O)_2]^{\cdot\cdot}$ (Bassett and Sanderson, J., 1932, 1861).

There can be no doubt from the general behaviour of the compounds that the thiosulphate is present as a complex anion. The evidence for $[Ag(S_2O_3)_2]'''$ seems fairly convincing (Bodländer, *Ber.*, 1903, **36**, 3933; Slator, J., 1905, **87**, 489). This may be



with 4-co-ordinated silver, though it is perhaps more likely that the silver is 2-co-ordinated and linked only to the two sulphur atoms. The fact that complex thiosulphates decompose to give trithionate in addition to heavy-metal sulphide (Bassett and Durrant, J., 1927, 1418) is strong evidence for such a structure for the complex anion, and the co-ordination number of the silver is of minor importance.

The complex formation must be attributed to the extra sulphur atoms of the thiosulphate ions, for sulphate ions have little tendency to form complexes—complex sulphates, as distinct from double sulphates, being very rare. For the latter reason it is unlikely that further linkages through oxygen atoms would occur to form chain anions containing more than one silver atom. It seems to follow from this that most of the compounds contain a portion of the silver in the kationic condition. The following constitutions appear to be the most likely for the four double salts dealt with in this paper.

(1) $Na^{\cdot}[Na_2(H_2O)_2]^{\cdot\cdot}[(S_2O_3)Ag(S_2O_3)]'''$
(2) $Na_3^{\cdot}[Na_2(H_2O)_2]^{\cdot\cdot}Ag^{\cdot}[(S_2O_3)Ag(S_2O_3)]_2'''$
(3) $[Na_2(H_2O)_2)]^{\cdot\cdot}Ag^{\cdot}[(S_2O_3)Ag(S_2O_3)]'''$
(4) $[Na_2(H_2O)_2]^{\cdot\cdot}Ag_4^{\cdot}[(S_2O_3)Ag(S_2O_3)]_2'''$

This constitutes a series of compounds containing the same complex anion but an increasing proportion of silver kations. On this basis the most probable constitution for silver thiosulphate itself would be $Ag_3^{\cdot}[(S_2O_3)Ag(S_2O_3)]'''$. The presence of free silver ion will cause instability in all cases, since it tends to settle on one of the sulphur atoms already attached to silver and so give rise to silver sulphide. Such action cannot readily occur with the dry solids, nor is it very liable to do so with compounds (1), (2), or (3) in contact with their equilibrium solutions. These contain sufficient excess of thiosulphate ions to immobilise most of the silver ions escaping from the solid by converting them into $[(S_2O_3)Ag(S_2O_3)]'''$ ions. Solutions from which compound (4) or silver thiosulphate can separate contain so few thiosulphate ions that this protective effect is hardly noticeable and rapid decomposition occurs.

EXPERIMENTAL.

Preparation of Starting Materials.—The salt $NaAg(S_2O_3),H_2O$ was used as starting material in all the experiments, and was prepared substantially according to Baines (*loc. cit.*, p. 2767). This author remarks that the reaction effected by sulphur dioxide is obscure. It seems probable that saturation of the solution with the gas brings about precipitation of $NaAg(S_2O_3),H_2O$ by destroying the excess of sodium thiosulphate which maintains it in solution, this salt being gradually converted into tri- or tetra-thionate (Bassett and Durrant, *loc. cit.*, p. 1440).

Suitable mixtures, about 10 g. in all, were prepared, by weighing, from $Na_2S_2O_3,5H_2O$, $NaAg(S_2O_3),H_2O$, and water. These were placed in hard-glass solubility bottles closed by waxed corks, and were shaken in a thermostat maintained at 25° ± 0·05° for 12 hours. A shorter time (minimum about ½ hour) had to be employed with the mixtures poor in sodium thiosulphate (see below).

The contents of the bottles were filtered through a jacketed filter tube, and solution and moist solid were then analysed. Total thiosulphate was estimated by titration with *N*/10-iodine. To determine silver, the material was treated with 50—100 c.c. of water and 5 c.c. of concentrated nitric acid, and the mixture simmered until it had become clear. Any sulphur remaining undissolved was liable to contain a little silver sulphide, and was filtered off, washed, and ignited, and the residue dissolved in a little nitric acid and added to the main solution. The silver was then titrated with standard potassium thiocyanate.

The percentages of sodium thiosulphate and silver thiosulphate were calculated from the results so obtained, and are recorded in the table and shown graphically in the Fig.

Satd. soln.		Moist solid.			Satd. soln.		Moist solid.		
$Na_2S_2O_3$,	$Ag_2S_2O_3$,	$Na_2S_2O_3$,	$Ag_2S_2O_3$,	Nature of solid phase.	$Na_2S_2O_3$,	$Ag_2S_2O_3$,	$Na_2S_2O_3$,	$Ag_2S_2O_3$,	Nature of solid phase.
%.	%.	%.	%.		%.	%.	%.	%.	
*43·15	0	63·70	0	α-$Na_2S_2O_3,5H_2O$	27·79	21·87	39·16	47·58	$Na_5Ag_3(S_2O_3)_4,2H_2O$
42·92	1·66	61·34	0·21	,,	27·56	21·91	34·06	56·29	Mixture point
43·06	5·50	60·84	0·84	,,	27·24	21·64	29·72	61·09	$NaAg(S_2O_3),H_2O$
42·99	7·07	58·14	1·89	,,	20·04	17·42	30·02	60·51	,,
43·31	7·30	55·10	13·93	Mixture point	12·54	10·98	29·39	61·24	,,
42·27	8·13	50·93	29·76	$Na_3Ag(S_2O_3)_2,2H_2O$	5·28	5·46	29·10	60·99	,,
41·48	8·90	51·22	30·98	,,	1·82	2·46	29·60	60·66	,,
38·28	12·52	51·64	32·48	,,	0·63	1·04	28·03	60·27	,,
36·49	15·81	50·38	32·96	,,	0·61	1·04	28·75	64·88	Mixture point
36·13	17·75	49·51	37·47	Mixture point	0·53	0·91	20·12	75·37	,,
35·98	17·76	48·96	36·86	,,	0·51	0·88	16·38	80·65	,,
33·90	18·62	40·43	42·48	$Na_5Ag_3(S_2O_3)_4,2H_2O$	0·43	0·75	13·91	82·10	$NaAg_3(S_2O_3)_2,H_2O$
32·40	19·36	38·08	37·28	,,	0·29	0·55	14·11	82·89	,,

* Young and Burke, *J. Amer. Chem. Soc.*, 1904, **26**, 1417.

Calculated compositions of double salts.

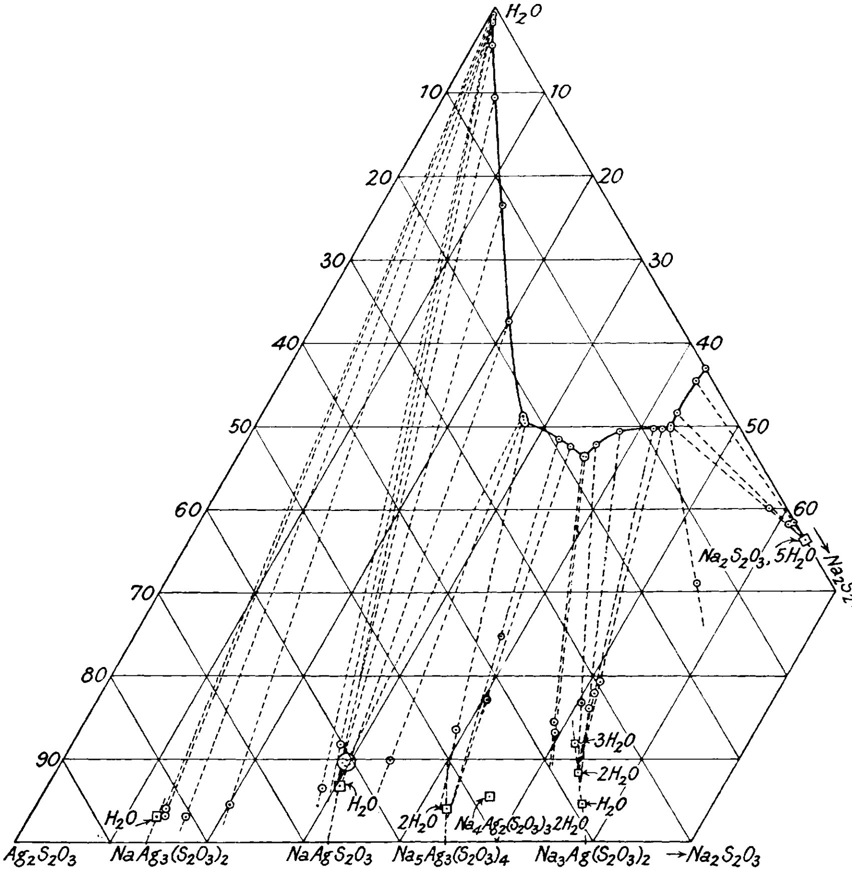
Double salt.	$Na_2S_2O_3$, %.	$Ag_2S_2O_3$, %.	H_2O, %.
$Na_3Ag(S_2O_3)_2,2H_2O$	54·26	37·50	8·24
$Na_5Ag_3(S_2O_3)_4,2H_2O$	42·83	53·28	3·89
$NaAg(S_2O_3),H_2O$	30·29	62·79	6·92
$NaAg_3(S_2O_3)_2,H_2O$	13·42	83·50	3·08

Difficulties due to Decomposition.—The major portion of the diagram presented no experimental difficulties, but when it no longer became necessary to add additional sodium thiosulphate to the $NaAg(S_2O_3),H_2O$ used in making up the solubility mixtures, decomposition manifested itself. The solubility mixtures lost their clean appearance after a few minutes, and became a dirty yellow-brown, owing to formation of colloidal silver sulphide.

The increasing insolubility and decomposition ultimately necessitated a number of special precautions in order that trustworthy results might be obtained. It was necessary to increase the volume of the solubility mixture to 200 c.c. and to decrease the time of shaking to ½ hour, the amount of $NaAg(S_2O_3),H_2O$ added being finally reduced to 2 g. As it was desirable, on account of decomposition, that the latter salt should dissolve and reach equilibrium as rapidly as possible, it was very finely ground in an agate mortar while the water, in the solubility bottle, was preheated to 25°. Sifting of the finely ground salt was unnecessary.

The mixture was vigorously and repeatedly shaken and placed in the thermostat at intervals during 20 minutes and finally shaken in the thermostat for 10 minutes.

The customary filtration apparatus could not be used, as the large volume of mixture and the presence of microscopic crystals and some colloidal silver sulphide rendered the filtration much too slow. The use of an ordinary Buchner funnel (previously heated a few degrees above the working temperature of 25°) with a hardened filter-paper supported on an ordinary one enabled filtration to be accomplished in about 6 minutes. The solid was rapidly dried by washing 3 times with a little absolute alcohol, followed by 3 washings with a little di*iso*propyl ether, and then dried at the pump for a few minutes while a portion of the filtrate was iodometrically analysed for thiosulphate as rapidly as possible on account of decomposition. The dry, finely divided solid could then be scraped off the hardened filter paper and analysed.



It was thus possible by rapid drying to prevent further decomposition of the solid, and to ascertain by analysis the composition of the dry solid phase $NaAg_3(S_2O_3)_2,H_2O$. The solubility curve of this compound is so short that the tie-lines are practically coincident, and it is impossible to determine the composition of the dry solid phase from their common point of intersection.

Washing with alcohol and ether did not alter the percentage composition of the dry solid. The amount of solid available for each analysis was small, a minimum of 0·05 g., so that it was necessary to use $N/100$-solutions for these analyses. On this account the best analytical results for the solid $NaAg_3(S_2O_3)_2,H_2O$ were liable to an error of about 1%.

When decomposition of the solubility mixture was more extensive, as indicated by the deeper colour, the iodometric titrations of the solid for total thiosulphate appeared to be too high. This was traced to the oxidation by iodine of a little colloidal silver sulphide filtered off along with the solid $NaAg_3(S_2O_3)_2,H_2O$, and when the duration of the experiment was reduced to a minimum so as to avoid this decomposition as far as possible, this disturbing factor disappeared within the limits of the experimental error.

Experiments with freshly prepared silver sulphide, thoroughly washed to ensure complete removal of hydrogen sulphide, indicated that it is oxidised by *N*/100-iodine to silver iodide and sulphur, but no sulphate could be detected. The reaction is fairly rapid until the small amount of colloidal and finely divided particles of sulphide has been oxidised; the coarser particles, after suffering superficial attack, then react slowly.

When the changes

$$\underset{\text{cryst.}}{NaAg(S_2O_3),H_2O} \longrightarrow \underset{\text{cryst.}}{NaAg_3(S_2O_3)_2,H_2O} \longrightarrow \underset{\substack{\text{white}\\ \text{gelatinous}}}{Ag_2S_2O_3} \longrightarrow \underset{\substack{\text{black}\\ \text{gelatinous}}}{Ag_2S}$$

produced by water acting upon finely ground $NaAg(S_2O_3),H_2O$ are observed under the microscope, it is seen that the ground rounded lumps of $NaAg(S_2O_3),H_2O$ commence to dissolve and diffuse into the surrounding water, producing concentric regions of increasing dilution. In the region of less dilution surrounding the central quantity of salt, very small square platelets of $NaAg_3(S_2O_3)_2,H_2O$ are rapidly deposited, and increase in number and size. In the more dilute regions, minute transparent gelatinous flecks, probably of insoluble silver thiosulphate, are produced, gradually increase in number and size, and darken to dirty yellow-brown and brown, as the silver thiosulphate decomposes to brownish-black silver sulphide. As diffusion proceeds the compounds richer in silver gradually encroach upon the areas occupied by the others until finally the only solid phase left consists of silver sulphide. These changes are much more rapid and marked in *N*/10-silver nitrate solution than in water. No sharp transition from the gelatinous insoluble silver thiosulphate to silver sulphide can be observed, nor does there appear to be any sodium silver thiosulphate richer in silver than $NaAg_3(S_2O_3)_2,H_2O$. This was further tested by preparing dry $NaAg_3(S_2O_3)_2,H_2O$, and treating it with water under the microscope, as above, but no formation of any other crystalline double salt could be observed.

One of us (J. T. L.) is indebted to the Department of Scientific and Industrial Research for a grant.

THE UNIVERSITY, READING. [*Received, July 7th,* 1933.]