

Instability Constant of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ at 25°, 35° and 45°

J. C. GHOSH

Department of Chemistry, Science College, Patna-5

Manuscript received 12 July 1973; accepted 19 October 1973

From the solubility of AgBr in aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solutions, it is found that the complex formed is $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ and pK of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} \rightleftharpoons \text{Ag}^+ + 2\text{S}_2\text{O}_3^{2-}$ is 13.83, 13.55 and 14.18 at 25°, 35° and 45°C, respectively.

THE reaction between Ag^+ and $\text{S}_2\text{O}_3^{2-}$ in solution to form complexes has been studied by a number of workers. Ferrel, Ridgion and Riley¹ found that instability constant of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ varied from 6.7×10^{-14} to 2.1×10^{-14} at room temperature. Chateau and Pouradier² from potentiometric measurements concluded that two complexes $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ having dissociation (instability) constants 3.5×10^{-14} and 7.0×10^{-15} respectively at 20° are formed when $\frac{[\text{Na}_2\text{S}_2\text{O}_3]}{[\text{Ag}^+]} > 2$. Later on³ they confirmed the existence of AgS_2O_3^- and found the dissociation constant 3.6×10^{-8} at 70°.

Dey⁴ studied the dissolution of AgBr (kept in excess) in $\text{Na}_2\text{S}_2\text{O}_3$ solution at 30°, 50° and 75° by a solubility method but he did not determine the instability constants. He concluded that at 30° the complex in solution is $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, at 75° it is $\text{Ag}(\text{S}_2\text{O}_3)^-$ and at 50° both the species are present.

It was therefore desirable to (i) study the composition of the complex formed between Ag^+ and $\text{S}_2\text{O}_3^{2-}$ and to (ii) determine the instability constant of the complex formed, at several temperatures.

Experimental

All chemicals used were of analytical grade. Water used was double distilled.

AgBr was prepared as follows: 25 g. of AgNO_3 dissolved in 500 ml water was acidified with 1 ml conc. HNO_3 . To this was added slowly a solution of KBr (50g/litre) till the precipitation was complete. The precipitate was heated to boiling and then allowed to stand for 1 hr in dark. Thereafter it was filtered through G-3 Jena sintered glass funnel. The precipitate was washed fifteen times with 0.5% HNO_3 and then heated to 150° for 2 hr and kept in desiccator. The whole process was carried out in a semidark room.

Standardisation⁵ KBrO_3 with showed that concentration of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution kept in dark did not change for a week. Calculated volume of standardised $\text{Na}_2\text{S}_2\text{O}_3$ solution was diluted to make 250 ml. solution of required strength at the temperature of the experiment and such solutions older than a day was not used.

In an apparatus designed for these experiments exactly 200 ml of $\text{Na}_2\text{S}_2\text{O}_3$ solution of known concentration was slowly circulated through a known weight of AgBr kept in a narrow sintered glass crucible. The thickness of silver bromide layer in the crucible was ca. 5 cm. Experiments were performed in an air thermostat maintaining 10.05°. Fifteen circulations were found to be enough to saturate the thiosulphate solution with silver bromide. The residual AgBr in the crucible was washed fifteen times with water followed by drying at 140° to constant weight. Duplicate experiments were run and the weight of AgBr dissolved agreed within 0.6 mg. (1.6×10^{-5} gm. mole/litre). Six sets of thiosulphate solutions to cover a range upto $\mu=0.1$ were used at each of the temperatures 25°, 35° and 45°.

At 25° and 35° the partially or completely saturated filtrate remained colourless for at least 4-5 days, while at 45° it darkened after 48 hours. Hence experiments at higher temperatures was not performed.

Results and Discussions

It is assumed that the reaction is $\text{Ag}^+ + n\text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_n^{-(2n-1)}$. When equilibrium has been attained,

$$[\text{AgBr}]_T = [\text{Ag}^+]_T = b$$

$$[\text{Na}_2\text{S}_2\text{O}_3]_T = [\text{S}_2\text{O}_3^{2-}]_T = d$$

$$\text{so, } [\text{Ag}^+] = \frac{K_{sp}}{\text{Br}^- f_+ f_-} = \frac{K_{sp}}{b \cdot f_+ f_-}$$

In the above equation f_+ and f_- are the activity coefficients of Ag^+ and Br^- , K_{sp} = solubility product of AgBr and $[K_{sp}]_T$ represents total concentration independent of the complex formed. Concentrations are in gm. moles/litre or g. atoms/litre.

$$[\text{Complex}] = \left(b - \frac{K_{sp}}{b \cdot f_+ f_-} \right) = b,$$

$$\text{and, } [\text{S}_2\text{O}_3^{2-}] = \left\{ d - n \left(b - \frac{K_{sp}}{b \cdot f_+ f_-} \right) \right\} = d - nb,$$

since $\frac{K_{sp}}{b f_+ f_-}$ is very small in comparison to either b or d .

The dissociation (instability) constant K is given as

$$\frac{1}{K} = \frac{[\text{Complex}] f}{[\text{Ag}^+] f_+ [\text{S}_2\text{O}_3^{2-}]^n f_{2-}} \dots \quad (1)$$

where, f = activity coefficient of complex and, f_{2-} = activity coefficient of $\text{S}_2\text{O}_3^{2-}$.

Taking activities equal to concentrations, we get

$$\frac{1}{K} = \frac{[\text{Complex}]}{[\text{Ag}^+] [\text{S}_2\text{O}_3^{2-}]^n} = \frac{b^2}{K_{sp} (d-2b)^n} \dots \quad (2)$$

Taking logarithms and rearranging we get

$$2 \log b = \log \frac{K_{sp}}{K} + n \log (d-2b) \dots \quad (3)$$

Both (2) and (3) are approximate equations. Tables 1, 2 and 3 show the experimental values of b and d and the related data at 25°, 35° and 45° respectively. In all these tables 'q' represents $2 \log b - 2 \log (d-2b) - 2A\sqrt{\mu}$.

Equilibrium stage in our experiments is very small (vide col. 3 of Tables 1, 2 and 3) $[\text{Na}_2\text{S}_2\text{O}_3]$, even if, present, is negligible. So, the ionic strength of the solution will be given by

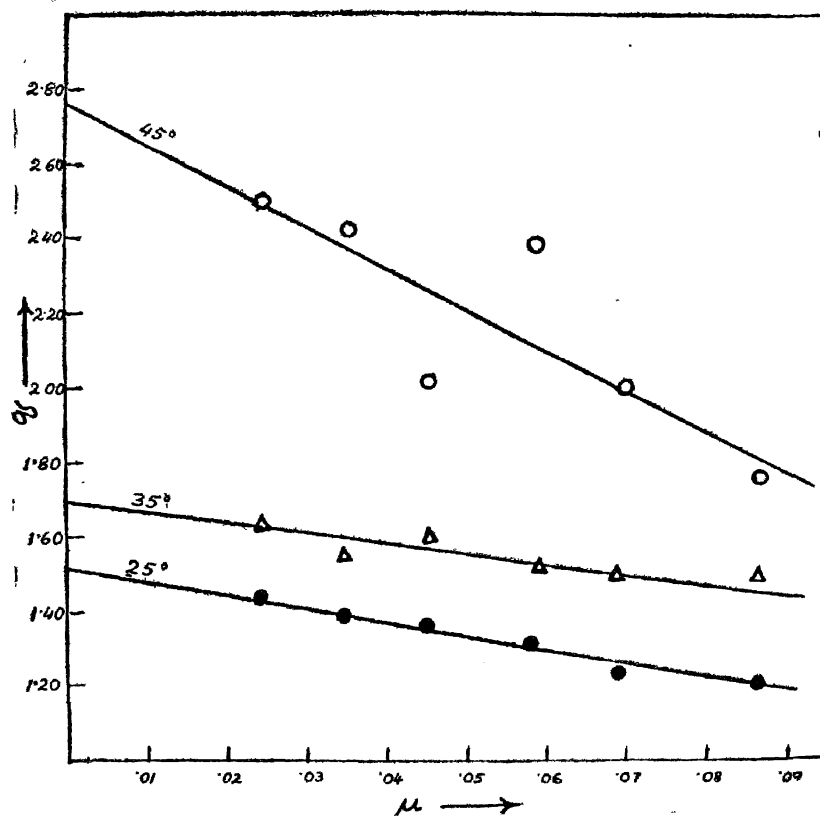
$$\begin{aligned} \mu &= \frac{1}{2} [\text{Ag}^+] + \frac{1}{2} [\text{Br}^-] + 2[\text{S}_2\text{O}_3^{2-}] + \frac{1}{2} [\text{Na}^+] + \frac{9}{2} [\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] \\ &= \frac{1}{2} \frac{K_{sp}}{b f_+ f_-} + \frac{1}{2} b + 2(d-2b) + \frac{2K_{sp}}{b f_+ f_-} \\ &+ \frac{1}{2} \cdot 2d + \frac{9}{2} \left(b - \frac{K_{sp}}{b f_+ f_-} \right) = 3d + b \dots \quad (4) \end{aligned}$$

Equation (1) may now be written as

$$\begin{aligned} \frac{1}{K} &= \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] f_{3-}}{[\text{Ag}^+] f_+ [\text{S}_2\text{O}_3^{2-}]^2 f_{2-}^2} \\ \text{or, } \frac{K_{sp}}{K} &= \frac{b^2 f_- f_{3-}}{(d-2d)^2 f_{2-}^2} \dots \quad (5) \end{aligned}$$

Taking logarithms and applying Debye-Huckel-Bronsted equation⁷ and rearranging, this reduces to

$$2 \log b - 2 \log (d-2b) - 2A\sqrt{\mu} = \log \frac{K_{sp}}{K} - \beta\mu \dots \quad (6)$$



Now we assign an arbitrary value to n in the expression $\log (d-2b)$ of equation (3) and plot $2 \log b$ against $2 \log (d-2b)$. When a plot is found to be a straight line with its slope almost equal to the assigned value of n we get an approximate value for n . Thus at 25°, 35° and 45° the value of n obtained was 1.9, 2.0 and 1.8 respectively i.e. ≈ 2 . Hence the amount of AgS_2O_3 seems to be negligible.

The formation of $\text{Na}_2\text{S}_2\text{O}_3$ and its dissociation constant have been reported⁶. Since $[\text{S}_2\text{O}_3^{2-}]$ at the equi-

A plot of L. H. S. of equation (6) denoted by q , against μ gives a straight line (fig. 1). The intercept on the ordinate is equal to $\log K_{sp}/K$. Utilising the recent value of K_{sp} on molarity scale as given by Jha and Prasad⁸, we get the value of pK as shown in Table 4. These values can be represented by the general equation

$$pK = \frac{1.33 \times 10^5}{T} - 855.3767 + 1.41917 T^2 \text{ and hence}$$

TABLE 1—DISSOLUTION OF Ag Br IN Na₂S₂O₃ AT 25°.

$d \times 10^3$	$b \times 10^3$	$\frac{(d-2b) \times 10^4}{10^4}$	$\frac{4+}{\log(d-2b)}$	$\frac{5+}{2 \log b}$	$\mu \times 10^2$	q
7.00	3.24	5.2	0.7160	0.0210	2.424	1.43
10.00	4.62	7.6	0.8808	0.3292	3.462	1.38
13.00	6.01	9.8	0.9912	0.5578	4.501	1.36
16.88	7.79	13.0	1.1139	0.7830	5.843	1.31
20.00	9.18	16.4	1.2148	0.9256	6.918	1.23
25.00	11.47	20.4	1.3096	1.1200	8.647	1.20

TABLE—2 DISSOLUTION OF Ag Br IN Na₂S₂O₃ AT 33°

$d \times 10^3$	$b \times 10^3$	$\frac{(d-2b) \times 10^4}{10^4}$	$\frac{4+}{\log(d-2b)}$	$\frac{5+}{2 \log b}$	$\mu \times 10^2$	q
7.00	3.29	4.2	0.6232	0.0344	2.429	1.63
10.00	4.68	6.4	0.8062	0.3404	3.468	1.54
13.00	6.12	7.6	0.8808	0.5736	4.512	1.59
17.10	8.08	10.5	1.0212	0.8094	5.932	1.51
20.00	9.38	12.4	1.0934	0.9444	6.938	1.49
25.00	11.75	15.0	1.1761	1.1400	8.675	1.48

TABLE 3—DISSOLUTION OF Ag Br IN Na₂S₂O₃ AT 45°.

$d \times 10^3$	$b \times 10^3$	$\frac{(d-2b) \times 10^4}{10^4}$	$\frac{4+}{\log(d-2b)}$	$\frac{5+}{2 \log b}$	$\mu \times 10^2$	q
7.00	3.42	1.6	0.2041	0.0680	2.442	2.50
10.00	4.88	2.4	0.3802	0.3768	3.488	2.42
13.00	6.26	4.8	0.6812	0.5932	4.526	2.01
17.00	8.30	4.0	0.6021	0.8382	5.930	2.38
20.00	9.65	7.0	0.8451	0.9690	6.965	2.00
25.00	11.95	11.0	1.0414	1.1548	8.695	1.76

ΔH in cal. is given by the equation,

$$\Delta H = 6.08475 \times 10^5 - 6.4927 T^2$$

Values of ΔH and ΔS thus calculated are also shown in Table 4.

TABLE 4—THERMODYNAMIC CONSTANTS FOR Ag

Temp. °C.	$\log \frac{K_{sp}}{K}$	$K_{sp} \times 10^{13}$	pK	$\frac{\Delta H}{K. cal./mole}$	ΔS e. u.
25	1.52	4.948	13.83	+31.12	+41.1
35	1.70	14.237	13.55	-8.25	-88.8
45	2.76	38.340	14.18	-48.92	-218.6

The valu of pK thus obtained and those reported in literature are summarised in Table 5.

TABLE 5—DISSOCIATION CONSTANT K OF

Author	Temp. °C	μ	pK	Remarks
Ferrel, Ridgion and Riley ¹	Room Temp.	—	13.36	Calculated from average K .
Chateau and Pouradier ²	20	—	13.46	
Kapoor ⁹	—	—	12.9	
This work	25	0	13.83	
"	35	0	13.55	
"	45	0	14.18	

It may be pointed out that similar experiments were carried out with AgCl. It was observed that AgCl started blackening in the course of experiment even at 35° when Na₂S₂O₃ solutions were used alone, but when mixtures of Na₂S₂O₃ and KCl were used there was no blackening. This clearly indicates that at higher concentration of Ag⁺ perceptible decomposition takes place. With rise in temperature also similar decomposition takes place. Our experiment with AgBr at 45° has not given as good a straight line as it has done at lower temperatures.

Acknowledgement

The author is thankful to Dr. B. Prasad, D. Sc, F. N. A., for his keen interest and helpful discussions

References

1. E. FERREL, J. H. RIDGION and H. L. RILEY, *J. Chem. Soc.*, 1936, 1121.
2. H. CHATEAU and J. POURADIER, *Science et inds phot.*, 1953, **24**, 20 ; *Chem. Abs.*, 1953, **47**, 6287.
3. H. CHATEAU and J. POURADIER, *Compt. Rend.*, 1955, **240**, 1882.
4. A. K. DEY, *J. Inorg. Nuclear. Chem.*, 1958, **6**, 71
5. A. I. VOGEL, *A Text Book of Quantitative Inorganic Analysis*, Longmans, 1962, p. 349.
6. T. O. DENNEY and C. B. MONK., *Trans. Faraday Soc.*, 1951, **47**, 992.
- 7 (i) J. N. BRONSTED and V. K. LAMER, *J. Amer. Chem. Soc.*, 1924, **46**, 555.
(ii) L. SHARMA, G. SAHU and B. PRASAD, *J. Indian Chem. Soc.*, 1968, **45**, 580.
8. A. C. JHA, *Ph. D. Thesis, Patna University*, 1972.
9. R. C. KAPOOR, *Proc. 60th Ind. Sc. Cong., Part II, Presidential Address*, 1973, p. 6.