

## SILVER HYPONITRITE: SOLUBILITY PRODUCT AND COMPLEXES IN AQUEOUS AMMONIA

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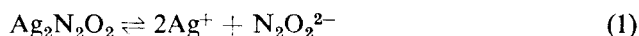
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**Abstract**—The solubility of silver hyponitrite in aqueous ammonia has been measured over the range of concentrations 0.1–2 N  $\text{NH}_3$ . The results are compatible with the assumption that the predominant complex formed in low concentrations is  $\text{Ag}(\text{NH}_3)_2^+$ . By addition of sodium hyponitrite the solubility of silver hyponitrite in ammonia (at a constant concentration) decreases first, but for moderate and higher concentrations of  $\text{Na}_2\text{N}_2\text{O}_2$  it increases again, showing the formation of the complex:  $(\text{NH}_3)\text{AgN}_2\text{O}_2^-$ . The instability constant of the latter is found to be approximately  $4 \times 10^{-9}$  at  $25.0^\circ$ , and the solubility product of  $\text{Ag}_2\text{N}_2\text{O}_2$   $1.30(\pm 0.15) \times 10^{-19}$  at the same temperature.

It has been pointed out by DIVERS<sup>(1)</sup> and many other investigators that silver hyponitrite is slightly soluble in concentrated solutions of hyponitrites and considerably soluble in aqueous ammonia. However nothing has been reported on the nature of the complexes formed, although dissolution of silver hyponitrite in ammonia and reprecipitation by mineral acids has been employed very often for purification purposes.

In view of the interesting structure of the ion  $\text{N}_2\text{O}_2^{2-}$ <sup>(2)</sup> and its possible mesomeric forms some attention should be paid to its co-ordination chemistry. Apart from the complex ion  $(\text{NH}_3)_5\text{Co})_2\text{N}_2\text{O}_2^{4+}$  studied by GRIFFITH<sup>(3)</sup> and earlier workers, there seems to be in the literature very little, if any, information on the co-ordination properties of  $\text{N}_2\text{O}_2^{2-}$ . We present here in brief the results of some solubility and e.m.f. measurements revealing the formation of the complex  $(\text{NH}_3)\text{AgN}_2\text{O}_2^-$  and we hope to be able in the future to provide some more data on the subject.

The method of investigating the composition of a complex by solubility measurements under suitable conditions was introduced by BODLÄNDER<sup>(4)</sup> who applied it to the dissolution of silver halides in ammonia. By similar arguments one would expect the equilibria



to be established in ammoniacal solutions saturated with  $\text{Ag}_2\text{N}_2\text{O}_2$ , with the constants

$$K_s = (\text{Ag}^+)^2(\text{N}_2\text{O}_2^{2-})$$

and

$$K_1 = (\text{Ag}^+)(\text{NH}_3)^2/(\text{Ag}(\text{NH}_3)_2^+)$$

<sup>(1)</sup> E. DIVERS, *J. Chem. Soc.* **75**, 95 (1899).

<sup>(2)</sup> L. KUHN and E. R. LIPPINCOTT, *J. Amer. Chem. Soc.* **78**, 1820 (1956); R. J. W. LE FÈVRE, W. T. OH, I. H. REECE and R. L. WERNER, *Australian J. Chem.* **10**, 361 (1957); D. J. MILLEN, C. N. POLYDOROPOULOS and D. WATSON, *J. Chem. Soc.* 687 (1960).

<sup>(3)</sup> W. P. GRIFFITH, J. LEWIS and G. WILKINSON, *J. Inorg. Nucl. Chem.* **7**, 38 (1958).

<sup>(4)</sup> G. BODLÄNDER and R. FITTIG, *Z. Phys. Chem.* **39**, 597 (1902).

respectively, where the parentheses stand for activities. Since the concentration of  $\text{Ag}^+$  is negligible, the soluble complex can be determined analytically. If its molality is  $C_0$ , by combining the two constants and inserting  $[\text{N}_2\text{O}_2^{2-}] = \frac{1}{2}[\text{Ag}(\text{NH}_3)_2^+] = C_0/2$  one obtains:

$$\log(f_{\pm} C_0) = \frac{1}{3} \log \left( \frac{2K_s}{K_1^2} \right) + \frac{4}{3} \log(\text{NH}_3) \quad (3)$$

where  $f_{\pm}$  is the mean activity coefficient of the electrolyte  $(\text{Ag}(\text{NH}_3)_2)_2\text{N}_2\text{O}_2$ . Therefore a plot of  $\log(f_{\pm} C_0)$  against  $\log(\text{NH}_3)$  is expected to be a straight line from which  $K_s$  could be evaluated.

At the same time the potential of a silver electrode immersed into the mixture is expected to drop linearly with increasing  $\log(\text{NH}_3)$  according to:

$$E = E_0 + \frac{2 \cdot 3RT}{3F} \log \frac{f_{\pm}}{f_{-}} + \frac{2 \cdot 3RT}{3F} \log(2K_s K_1) - \frac{2 \times 2 \cdot 3RT}{3F} \log(\text{NH}_3) \quad (4)$$

On the other hand addition of a soluble hyponitrite ( $\text{Na}_2\text{N}_2\text{O}_2$ ) at constant ammonia concentration would reduce the silver content of the solutions, as it displaces both equilibria to the left, if there were no other reactions taking place.

As it will be seen, however, the results of the measurements can not be interpreted in terms of these two reactions only.

#### EXPERIMENTAL

Sodium hyponitrite was prepared by the method of Divers-Partington (discussed elsewhere<sup>(5)</sup>) with the modification that the sodium amalgam was prepared electrolytically in a cell similar to that described by ABEL<sup>(6)</sup>. The silver hyponitrite obtained by precipitation of the raw material was purified by reprecipitation from cold 0.1 N nitric acid. The solutions of sodium hyponitrite used for measurements were prepared by the action of pure silver hyponitrite (not dried) on a solution of NaI.

All solubility and e.m.f. measurements were made at  $25.0 \pm 0.1^\circ\text{C}$ . The solutions were left to establish equilibrium with some solid  $\text{Ag}_2\text{N}_2\text{O}_2$  at this temperature for about six hours. Any longer treatment might have caused serious errors due to the decomposition of hyponitrites.\* Filtration (for sampling out) was effected by exerting pressure on the mixtures, being still kept in the thermostat.

The solutions contained always some NaOH (0.1-0.2 N) to avoid any considerable hydrolysis of  $\text{N}_2\text{O}_2^{2-}$ ,<sup>(5)</sup> as well as to stabilize it as far as possible.<sup>(6)</sup>

The silver content of the samples was determined volumetrically (KSCN) after acidification with  $\text{HNO}_3$ . For the determination of the total  $\text{N}_2\text{O}_2^{2-}$  in solution, silver nitrate was added (if necessary) in small excess, the solution was brought to a pH 5-6, and the precipitate ( $\text{Ag}_2\text{N}_2\text{O}_2$ ) washed, dissolved in  $\text{HNO}_3$  and titrated with KSCN.

The silver electrode potentials were measured by means of the set:

(—) Saturated calomel electrode ||  $\text{KNO}_3$  || solution tested |  $\text{Ag}(+)$  immersed in the thermostat. The indicator electrode was silver-plated silver. It was standardized in the same cell repeatedly against 0.1 N  $\text{AgNO}_3$  in which the activity coefficient of  $\text{Ag}^+$  was taken as 0.82. The potentiometer was calibrated against a certificated Weston cell. The average uncertainty of the measurements was  $\pm 1.5$  mV.†

\* In a series of measurements the apparent solubility of silver hyponitrite in 0.45 M  $\text{NH}_3$  was found to change by 2-3% between 1 and 5 hr after the preparation of the mixtures. Between 5 and 10 hr no change in the solubility was detectable. After 24 hr treatment a sample was found to have decomposed by 17 per cent.

† A higher accuracy was not attempted since, unfortunately, the accuracy in a work on hyponitrites is anyhow limited by two factors: (a) their instability and (b) lack of sufficient literature on even the most elementary points of the chemistry of hyponitrites, e.g. their quantitative determination.

<sup>(5)</sup> C. N. POLYDOROPOULOS, *Chim. Chronika* 24 A, 147 (1959).

<sup>(6)</sup> E. ABEL and J. PROISL, *Wien. Mh.* 72, 1 (1938).

TABLE 1.—SOLUBILITY OF SILVER HYPONITRITE IN AQUEOUS AMMONIA

(NH <sub>3</sub> )	C <sub>0</sub>	NaOH (molal)	μ	f <sub>±</sub>	f <sub>±</sub> C <sub>0</sub>	E <sub>0</sub> ' - E (mV)
0.091	0.262	0.099	0.103	0.59	0.155	456
0.192	0.728	0.099	0.110	0.58	0.422	463
0.495	2.65	0.100	0.140	0.56	1.48	486
0.827	5.56	0.198	0.281	0.48	2.67	491
0.952	6.67	0.102	0.202	0.52	3.47	502
1.444	11.26	0.103	0.272	0.49	5.52	515

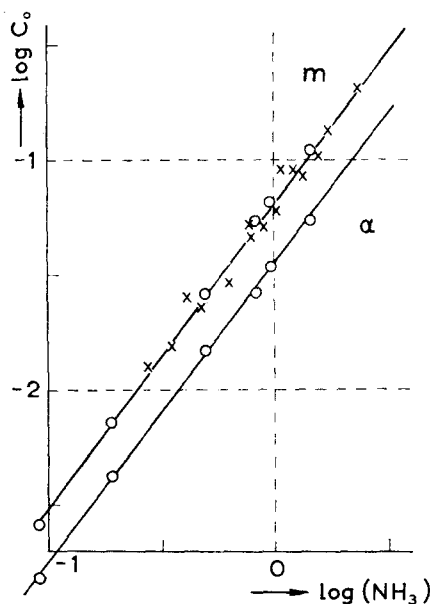


FIG. 1.—Solubility of silver hyponitrite in aqueous ammonia. The points shown by × have been determined less accurately.

## RESULTS

### (a) Variation of activity coefficients with ionic strength

Increasing amounts of KNO<sub>3</sub> were added in a series of solutions saturated with Ag<sub>2</sub>N<sub>2</sub>O<sub>2</sub> at constant 0.45 M NH<sub>3</sub> and 0.1 N NaOH. The increase of the solubility with increasing ionic strength (up to μ = 0.45) showed a dependence of the form

$$-\log f_{\pm} = \frac{2A\sqrt{\mu}}{1 + \alpha B\sqrt{\mu}} \quad (5)$$

(where  $A = 0.51$  and  $B = 3.29 \times 10^7$ ) and an effective diameter of the ions involved  $\alpha = 4.0 \times 10^{-8}$ .

### (b) Solubility of silver hyponitrite in ammonia

This is shown by table and Fig. 1 where C<sub>0</sub> is the total molality of silver containing soluble compounds (in equiv. of Ag) and (NH<sub>3</sub>) is the molality of free ammonia i.e. the difference of 2C<sub>0</sub> from the total ammonia according to equation (2).

In Fig. 1 curve  $m$  shows  $\log C_0$ , whereas curve  $\alpha$  shows  $\log (f_{\pm} C_0)$  against  $\log (\text{NH}_3)$ . The latter seems to be in good agreement with equation (3). The activity coefficients were calculated by means of (5).

The slope of the experimentally found straight line  $\alpha$  is  $1.30 \pm 0.02$  as compared to 1.33 predicted by equation (3). Furthermore the value of the constant term in (3) is found to be  $-1.435 \pm 0.015$ . Taking  $K_1 = 7.86 \times 10^{-8}$  (RANDALL<sup>(7)</sup>) one finds\*  $K_s = 1.53 \pm 0.16 \times 10^{-19}$ .

The potential of a silver electrode in aqueous ammonia saturated with silver hyponitrite should follow equation (4).

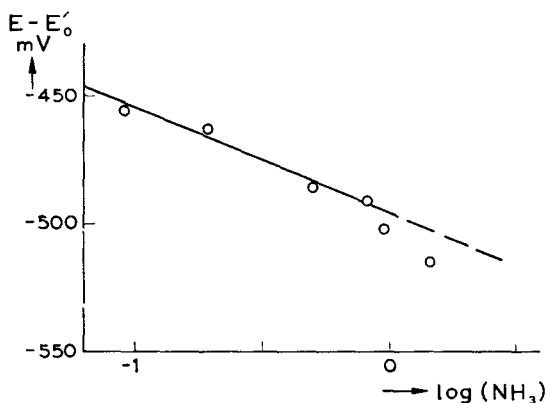


FIG. 2.—Silver electrode potential in aqueous ammonia saturated with silver hyponitrite.

Fig. 2 shows a plot of  $E - E_0'$  against  $\log (\text{NH}_3)$ , where  $E_0'$  is the potential of the same cell for  $(\text{Ag}^+) = 1$ . For moderate concentrations the slope of the curve obtained is very near to 40 mV as expected, but it deviates at higher concentrations. This probably occurs because the ratio of the two activity coefficients involved in equation (4) does not remain constant for a wide region of ionic strengths (see Table 1) ( $f_{\pm}$  is the activity coefficient of a univalent cation, and  $f_-$  that of a bivalent anion). Besides at higher concentrations the formation of another complex  $(\text{NH}_3\text{AgN}_2\text{O}_2^-)$  would have to be taken into account, as shown below.

(c) *Solubility of  $\text{Ag}_2\text{N}_2\text{O}_2$  in soluble hyponitrite at constant ammonia concentration*

The effect of the presence of sodium hyponitrite on the solubility of silver hyponitrite is shown in Table 2.  $[\text{Ag}]$  is the total molality of silver complexes in equiv. of Ag. For  $(\text{NH}_3) \neq 0$ ,  $C_0$  is the molality of ammoniacal silver complexes, i.e.  $[\text{Ag}]$  corrected by subtraction of the solubility for the same concentration of  $\text{Na}_2\text{N}_2\text{O}_2$  and  $(\text{NH}_3) = 0$ .

If only reactions (1) and (2) were to be considered,  $C_0$  would be the molality of  $\text{Ag}(\text{NH}_3)_2^+$  and

$$f_{\pm} C_0 = 1/K_1 (\text{NH}_3)^2 (\text{Ag}^+)$$

\* A correction to allow for the formation of  $\text{AgNH}_3^+$  would lie well within the limits of the experimental error since the formation constant  $k_2 = (\text{Ag}(\text{NH}_3)_2^+)/(\text{AgNH}_3^+(\text{NH}_3))$  is  $7.8 \times 10^3$  and therefore the ratio of the two complexes can not be smaller than  $7.8 \times 10^3 \times 0.091 = 7.1 \times 10^2$  in the region of ammonia concentrations used.

<sup>(7)</sup> M. RANDALL and J. O. HALFORD, *J. Amer. Chem. Soc.* **52**, 178 (1930).

TABLE 2.—SOLUBILITY OF  $\text{Ag}_2\text{N}_2\text{O}_2$  IN  $\text{Na}_2\text{N}_2\text{O}_2$  AT CONSTANT AMMONIA CONCENTRATION\*

$[\text{N}_2\text{O}_2^{2-}]$	$[\text{Ag}]$	$C_0$	$[\text{NaOH}]$	$\mu$	$f_{\pm}$	$f_{\pm} C_0$	$E_0' - E$ (mV)
			( $\text{NH}_3$ ) = 0				
0.0311	$\times 10^{-2}$ 0.055		0.270	0.364			
0.0496	0.094		0.293	0.443			
0.321	1.20		0.683	1.66			
0.673	1.96		1.231	3.28			
			( $\text{NH}_3$ ) = 0.31				
0.0069	1.38	$\times 10^{-2}$ 1.37	0.100	0.121	0.75	$\times 10^{-2}$ 1.03	474
0.0138	0.87	0.84	0.063	0.100	0.77	0.65	499.3
0.0303	0.97	0.91	0.069	0.151	0.74	0.67	505.8
0.0628	1.19	1.06	0.091	0.268	0.70	0.74	515.8
0.139	1.64	1.40	0.113	0.514	0.65	0.91	524.3
			( $\text{NH}_3$ ) = 0.88				
0.028	5.56	5.50	0.198	0.28	0.69	3.80	491
0.100	5.15	5.00	0.092	0.34	0.68	3.40	513
0.200	6.30	5.80	0.193	0.73	0.63	3.66	520
0.402	8.19	6.80	0.378	1.50	0.58	3.95	523

\*  $C_0$  = molalities and  $f_{\pm} C_0$  = activities of silver-ammonia complexes.

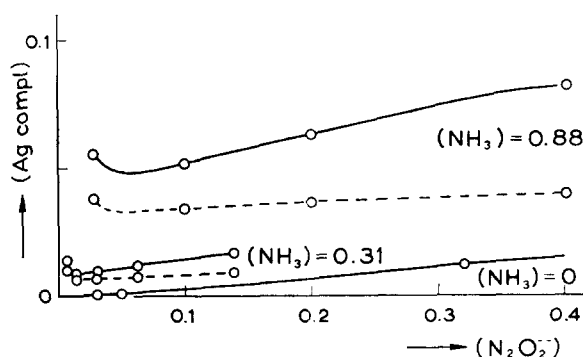


FIG. 3.—Solubility of  $\text{Ag}_2\text{N}_2\text{O}_2$  in  $\text{Na}_2\text{N}_2\text{O}_2$  at constant ammonia concentration. Continuous lines show molalities. Dotted lines show  $f_{\pm} C_0$ .

That the activity of free silver ions decreases is shown by the drift in the electrode potential. If  $f_{\pm}$  is calculated from (5) for a univalent ion of  $\alpha = 4.0 \times 10^{-8}$ , then  $f_{\pm} C_0$  decreases first and at higher concentrations of  $\text{Na}_2\text{N}_2\text{O}_2$  it increases again, (Fig. 3). Therefore at least one more reaction apart from (1) and (2) must be considered.

(d) *The solubility product of silver hyponitrite*

To make sure that equilibrium (1) is established the silver electrode potential was measured in a series of sodium hyponitrite solutions in equilibrium with  $\text{Ag}_2\text{N}_2\text{O}_2$

(Fig. 4). A small correction was made to the molality of  $\text{N}_2\text{O}_2^{2-}$  to allow for the formation of silver-hyponitrito complexes according to Table 2.

$E$  is expected to be a linear function of  $\log (\text{N}_2\text{O}_2^{2-})$  according to:

$$E = E_0' + \frac{2.3RT}{2F} \log \frac{K_s}{f_-} - \frac{2.3RT}{2F} \log (\text{N}_2\text{O}_2^{2-})$$

with a slope of 29.5 mV, provided there is no considerable variation in  $f_-$  (the activity coefficient of  $\text{N}_2\text{O}_2^{2-}$ ).

The straight line shown in Fig. 4 was drawn at a slope 29.5 mV. The points of measurements do not seem to deviate considerably.

For  $[\text{N}_2\text{O}_2^{2-}] = 0.01$ ,  $E - E_0'$  is found to be  $-485.8 \pm 2$  mV. Thus  $K_s' = K_s/f_- = 3.7 \pm 0.4 \times 10^{-19}$  for  $\mu \cong 0.15$ .

If  $f_- = 0.30^*$ ,  $K_s$  would be  $1.11 \pm 0.12 \times 10^{-19}$ .

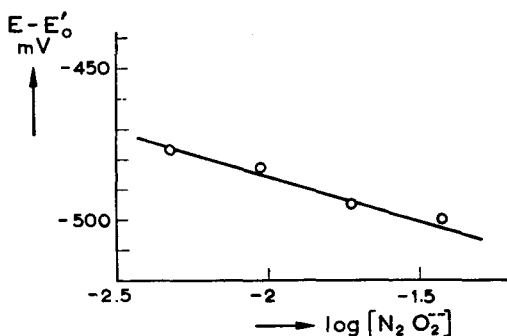


FIG. 4.—Silver electrode potential in  $\text{Na}_2\text{N}_2\text{O}_2$  solution in equilibrium with  $\text{Ag}_2\text{N}_2\text{O}_2$ .

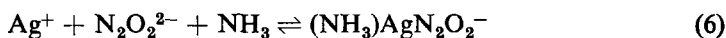
#### DISCUSSION

To draw conclusions, as to what substances are formed when silver hyponitrite dissolves in aqueous ammonia, the most characteristic of all series of measurements are those in Fig. 3. Evidently the simplest interpretation of the curves obtained is that they represent the sum of two functions, one hyperbolic and one parabolic. The hyperbola corresponds to the solubility of  $\text{Ag}_2\text{N}_2\text{O}_2$  in the form of  $\text{Ag}(\text{NH}_3)_2^+$ , the molality of which ( $C_1$ ) is expected to fall with increasing  $\text{N}_2\text{O}_2^{2-}$  according to:

$$C_1 = \frac{1}{f_1} \times \frac{K_s^\dagger}{K_1} \times \frac{(\text{NH}_3)^2}{(\text{N}_2\text{O}_2^{2-})^\dagger}$$

where  $f_1$  is its act. coefficient.

The parabola indicates the formation of at least one more silver complex. Its concentration seems (by Fig. 3) to be proportional to  $(\text{N}_2\text{O}_2^{2-})^\dagger$  (for  $(\text{NH}_3) = \text{const.}$ ) and to  $(\text{NH}_3)$  (for  $(\text{N}_2\text{O}_2^{2-}) = \text{const.}$ ). These requirements are satisfied if the reaction



is assumed to take place together with (1) and (2). If it is so, the molality of this complex ( $C_2$ ) would be:

$$C_2 = \frac{1}{f_2} \times \frac{K_s^\ddagger}{K_2} \times (\text{NH}_3) \times (\text{N}_2\text{O}_2^{2-})^\dagger$$

\* Calculated from (5) for  $\alpha = 4.0 \times 10^{-8}$  and  $\mu = 0.15$ .

where  $K_2$  is the instability constant

$$K_2 = (\text{Ag}^+)(\text{N}_2\text{O}_2^{2-})(\text{NH}_3)/(\text{NH}_3\text{AgN}_2\text{O}_2^-).$$

Thus  $C_0$ , determined volumetrically, would be the sum of the two complexes ( $C_0 = C_1 + C_2$ ) and if it is assumed that the activity coefficients of the two complex ions are very nearly equal, and if they are replaced by  $f_{\pm}$ , it follows

$$\frac{f_{\pm} C_0}{(\text{Ag}^+)} = \frac{(\text{NH}_3)^2}{K_1} + \frac{(\text{NH}_3)K_s}{K_2} \times \frac{1}{(\text{Ag}^+)^2}$$

where the activity of ammonia has been substituted by its molality after RANDALL<sup>(8)</sup>. Therefore a plot of  $f_{\pm} C_0/(\text{Ag}^+)$  against  $1/(\text{Ag}^+)^2$  should be a straight line from the slope of which the ratio  $K_s/K_2$  could be estimated. This is calculated in Table 3 from the data of Table 2 and shown by Fig. 5.

TABLE 3.

$f_{\pm} C_0$	$E_0' - E$ (mV)	$\frac{1}{(\text{Ag}^+)}$	$\frac{1}{(\text{Ag}^+)^2}$	$\frac{f_{\pm} C_0}{(\text{Ag}^+)}$
		(NH <sub>3</sub> ) = 0.31		
$\times 10^{-2}$		$\times 10^8$	$\times 10^{16}$	$\times 10^6$
1.03	474	1.02	1.04	1.05
0.65	499.3	2.76	7.61	1.79
0.67	505.8	3.56	12.7	2.40
0.74	515.8	5.25	27.6	3.90
0.91	524.3	7.31	53.5	6.65
		(NH <sub>3</sub> ) = 0.88		
$\times 10^{-2}$		$\times 10^8$	$\times 10^{17}$	$\times 10^7$
3.80	491	2.04	0.416	0.774
3.40	513	4.79	2.30	1.63
3.66	520	6.31	3.99	2.31
3.95	523	7.08	4.96	2.80

The slope of the functions in Fig. 5 is  $4.32 \times 10^{-11}$  for (NH<sub>3</sub>) = 0.88, and  $1.06 \times 10^{-11}$  for (NH<sub>3</sub>) = 0.31. Thus  $K_2/K_s$  is found  $2.04 \times 10^{10}$  and  $2.93 \times 10^{10}$  respectively.

From the intercept the value of  $K_1$  is found  $12.5 \times 10^{-8}$  (for (NH<sub>3</sub>) = 0.88) and  $10 \times 10^{-8}$  (for (NH<sub>3</sub>) = 0.31). Its actual value is  $7.86 \times 10^{-8}$ .

The inconsistency is probably due to the assumption made that  $f_1 = f_2 = f_{\pm}$ .

The series for (NH<sub>3</sub>) = 0.31 seems more reliable as it involves moderate ionic strengths and it yields a value for  $K_1$  nearer to the correct one. Therefore  $K_2$  can be taken as approximately equal to  $3 \times 10^{10} K_s$ , and this should not be in error by more than 30 per cent.

It seems therefore that there can be little doubt about the existence of equilibrium (6) in solutions of silver hyponitrite in ammonia. Even without addition of sodium hyponitrite, silver hyponitrite dissolves in aqueous ammonia to form  $\text{NH}_3\text{AgN}_2\text{O}_2^-$  at a considerable extent as compared to the classical  $\text{Ag}(\text{NH}_3)_2^+$ . Thus a calculation of the ratio  $\text{Ag}(\text{NH}_3)_2^+/\text{NH}_3\text{AgN}_2\text{O}_2^-$  (which must be very nearly equal to  $K_2/K_1K_s$

<sup>(8)</sup> M. RANDALL and J. O. HALFORD, *J. Amer. Chem. Soc.* **52**, 192 (1930).

$(\text{NH}_3)(\text{Ag}^+)^2$  based on the dependence of  $E$  on the concentration of  $\text{NH}_3$  (Fig. 2), shows that, even in 0.2 N  $\text{NH}_3$ , the concentration of  $\text{Ag}(\text{NH}_3)_2^+$  is only twenty times as high as that of  $(\text{NH}_3)\text{AgN}_2\text{O}_2^-$ , and that their ratio decreases down to 1.2 in 2 N  $\text{NH}_3$ .

Thus the value  $K_s = 1.53 \times 10^{-19}$  from Fig. 1 should be considered only as an upper limit as its calculation was made with the assumption that only the complex  $\text{Ag}(\text{NH}_3)_2^+$  is formed. On the other hand the value  $1.11 \times 10^{-19}$  from Fig. 4 may be

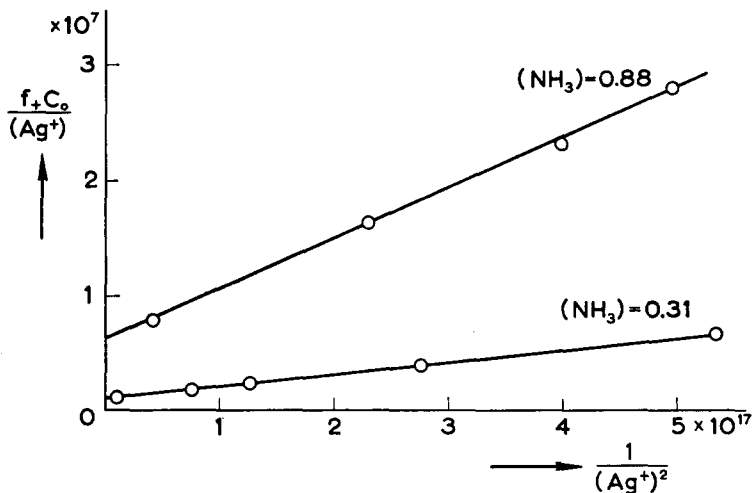


FIG. 5.—Illustration of the linear relationship between  $f_{\pm} C_0 / (\text{Ag}^+)$  and  $1 / (\text{Ag}^+)^2$ .

too low as the activity coefficient of  $\text{N}_2\text{O}_2^{2-}$  for  $\mu = 0.15$  was taken  $f_- = 0.30$ . Higher  $f_-$  would seem more reasonable, e.g. 0.35 which would lead to a  $K_s = 1.30 \times 10^{-19}$ . This is actually the mean of 1.53, 1.11 and  $1.22 \times 10^{-19}$  the last of which was calculated (as not shown here) from the measurements connected with the establishment of relationship (5). Thus we take as most reliable  $K_s = 1.30 \pm 0.15 \times 10^{-19}$  and consequently  $K_2 \cong 4 \times 10^{-9}$ .

A great deal of work has been devoted to the preparation and study of silver complexes with various ligands. As a rule the ligands (usually two) coordinated to a  $\text{Ag}^+$  are always identical or at least very similar. Comparatively, only a few cases of detection of silver complexes with different ligands have been reported, e.g.  $\text{AgNH}_3\text{PO}_4^{2-}$ <sup>(9)</sup>,  $\text{Ag}(\text{NH}_3)_2(\text{CrO}_4)^{3-}$  and  $\text{Ag}(\text{NH}_3)_2\text{CrO}_4^{-}$ <sup>(10)</sup>,  $\text{Ag}(\text{NH}_3)_2\text{X}_2^-$  where  $\text{X}^- = \text{BrO}_3^-$ ,  $\text{IO}_3^-$ , or  $\text{Cl}^-$ <sup>(11)</sup> etc. Thus the data presented above may also be found useful to the study of the properties of silver ion.

*Acknowledgement*—The authors gratefully acknowledge the support of this work by the Royal Hellenic Research Foundation.

<sup>(9)</sup> H. C. SARASWAT, *Proc. Indian Acad. Sci.* **30 A**, 329 (1949).

<sup>(10)</sup> M. B. SHCHIGOL and S. M. BIRNBAUM, *Zavodskaya Lab.* **15**, 1027 (1949) and *Chem. Abstr.* **44**, 1362 f (1950).

<sup>(11)</sup> M. B. SHCHIGOL, *Zh. Obshchei Khim.* **22**, 721 (1952); *J. Gen. Chem. U.S.S.R.* (Engl. transl.) **22**, 787 (1952) and *Chem. Abstr.* **47**, 3167 c (1953).