

## Anionic Silver Iodide Complexes in Aqueous Solutions

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The reaction between solid silver iodide and iodide ions was studied by solubility measurements at 25° C and at an ionic strength of 4 M (NaClO<sub>4</sub>). The results have been interpreted by assuming that the mononuclear species AgI<sub>n</sub><sup>1-n</sup> (*n* = 1, 2, 3, and 4) and the polynuclear species Ag<sub>2</sub>I<sub>3</sub><sup>-</sup> and Ag<sub>3</sub>I<sub>5</sub><sup>-</sup> were formed. At the highest iodide concentrations the saturated solutions also contained other more highly charged species. Their composition could not be determined exactly, but they are of the form (AgI<sub>2</sub>)<sub>*m*</sub> or closely similar, most probably Ag<sub>*m*</sub>I<sub>2*m*+2</sub><sup>(*m*+2)-</sup>, with rather high average values of *m* (~10).

Earlier measurements of the solubility, *l*, of silver iodide have been summarized by Sillén<sup>1</sup>, and a survey of equilibrium constants for the silver iodide system is given by Kratochvíl, Težák, and Vouk<sup>2</sup>. King, Krall, and Pandow<sup>3</sup> are the only authors who have used a constant ionic strength (2 M NaClO<sub>4</sub>). Their method was a direct titration analysis, which could only be used when *l* > ~10<sup>-4</sup>. Their results can be described by eqn. (2) below. The constants in this equation have been calculated by the author for the range of their data, *vide* Table 2. They agree, after making a reasonable allowance for the difference in ionic strength, with those I have now determined.

The solubility of silver iodide in the solvent *c*<sub>NaI</sub> M NaI + (4 - *c*<sub>NaI</sub>) M NaClO<sub>4</sub>, where *c*<sub>NaI</sub> ranged from 5 × 10<sup>-4</sup> to 4, was determined in the following ways: by electroanalyses after addition of sodium cyanide, when *l* > 10<sup>-3</sup>; by potentiometric microtitrations with bromide (*vide* Ref.<sup>4</sup>) in the range 10<sup>-6</sup> < *l* < 10<sup>-2</sup>; and by a radio assay technique, with silver iodide labelled with <sup>110</sup>Ag (from Harwell), when *l* < 10<sup>-4</sup>. The solubility equilibria were in all cases established in less than one day. Experimental details are given elsewhere (Refs.<sup>5-8</sup>). The results are collected in Table 1. The accuracy has been judged from the reproducibility of the experiments. Every solubility given in Table 1 has been determined at least three times, several of them more than five times. The poor accuracy at low solubilities depends mainly on the small specific activity. When the solubility could be determined by two methods they were always in agreement. The original concentrations of sodium iodide in the solvent were corrected for the change in volume at saturation. This correction became significant at the highest solubilities measured.

Table 1. The solubility,  $l$  (in  $M$ ), of silver iodide in aqueous sodium iodide. Ionic strength of the solvent  $4 M$  ( $NaClO_4$ ) except in the last one ( $6 M NaI$ ).

CNaI	$l$	CNaI	$[I^-]$ **	$l$
$5 \times 10^{-4}$	$(7 \pm 1) \times 10^{-9}$	0.8 *	0.78	$(198 \pm 1) \times 10^{-4}$
$10^{-3}$	$(13 \pm 1) \times 10^{-9}$	1.00 *	0.95	$(187 \pm 5) \times 10^{-4}$
$2 \times 10^{-3}$	$(3 \pm 1) \times 10^{-8}$	1.20 *	1.12	$(347 \pm 1) \times 10^{-4}$
$5 \times 10^{-3}$	$(8 \pm 2) \times 10^{-8}$	1.50 *	1.35	$(696 \pm 3) \times 10^{-4}$
0.01	$(33 \pm 3) \times 10^{-8}$	1.75 *	1.51	$0.110 \pm 0.001$
0.02	$(112 \pm 5) \times 10^{-8}$	2.00 *	1.65	$0.168 \pm 0.001$
0.05	$(77 \pm 1) \times 10^{-7}$	2.25	1.78	$0.238 \pm 0.001$
0.08	$(214 \pm 5) \times 10^{-7}$	2.46	1.85	$0.323 \pm 0.001$
0.1	$(35 \pm 1) \times 10^{-6}$	2.74	1.97	$0.437 \pm 0.002$
0.2	$(20 \pm 1) \times 10^{-5}$	2.93	2.03	$0.528 \pm 0.003$
0.3	$(59 \pm 2) \times 10^{-5}$	3.85	2.23	$1.08 \pm 0.01$
0.5 *	$(24 \pm 1) \times 10^{-4}$	5.46	2.37	$2.41 \pm 0.01$

\* In these 7 solutions the concentration of free iodide ions could be determined by e. m. f. measurements, which gave the following results for  $[I^-]$ : 0.49, 0.78, 0.95, 1.11, 1.35, 1.50, 1.7 respectively.

\*\* Calculated from eqn. (5).

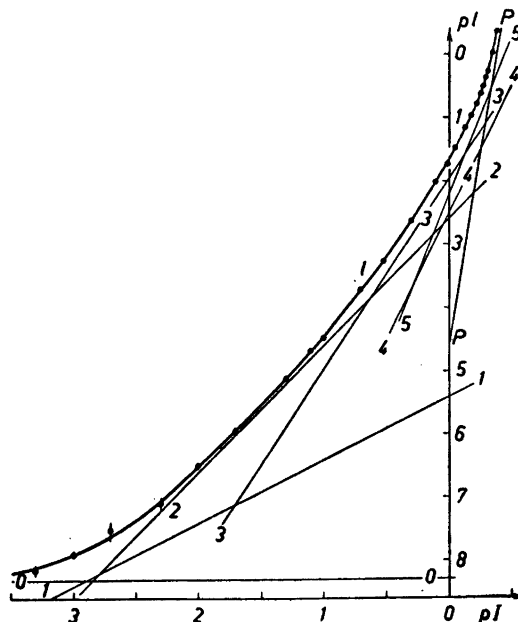
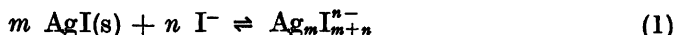


Fig. 1. The solubility,  $l$ , of silver iodide in aqueous sodium iodide. The numbered straight lines give the concentration of silver in the respective complexes as follows: 0:  $AgI$ , 1:  $AgI_2^-$ , 2:  $AgI_3^{2-}$ , 3:  $AgI_4^{3-}$ , 4:  $Ag_2I_5^{4-}$ , 5:  $Ag_3I_6^{5-}$ .  $P$  signifies the entire silver contents in species of ionic weight greater than  $Ag_3I_6^{5-}$ . Ionic strength  $4 M$  ( $NaClO_4$ ).

The dissolution of solid silver iodide in aqueous sodium iodide depends on reactions of the type



where  $m$  and  $n$  are integers to be determined by experiment. Hence the solubility is described by (cf. Ref.<sup>4</sup>)

$$l = \sum_{n=-1}^N K_n [\text{I}^-]^n \quad (2)$$

If there is only one species of charge  $-n$ , it follows that

$$K_n = m \cdot k_{m,n} \quad (3)$$

where  $k_{m,n}$  is the equilibrium constant for reaction (1). If there are several

species with the same charge, eqn. (3) would become  $K_n = \sum_{m=1}^M m \cdot k_{m,n}$ .

*Computation of the constants  $K_n$ .*  $K_0$  has been determined previously from measurements of the solubility of silver iodide in aqueous silver perchlorate at 25°C and at an ionic strength of 4 M ( $\text{NaClO}_4$ ), Ref.<sup>8</sup>; the value  $K_0 = (6 \pm 1) \times 10^{-9}$  was found. This value ought to be confirmed by corresponding measurements with  $^{110}\text{Ag}$  at low iodide concentrations, but the maximum specific activity of the silver obtainable at Harwell, is just insufficient to measure concentrations in the range  $10^{-9}$  M with the apparatus at my disposal. The first term,  $K_{-1}/[\text{I}^-]$ , of eqn. (2) is negligible in all solutions studied in this paper as the solubility product  $K_{-1} = 4.5 \times 10^{-17}$  (cf. Refs.<sup>8,9</sup>).

In the range  $5 \times 10^{-3} \leq [\text{I}^-] \leq 5 \times 10^{-2}$ ,  $l$  is rather well described by a straight line of slope 2 in a logarithmic diagram (*vide* Fig. 1), which means that the term  $K_2[\text{I}^-]^2$  of eqn. (2) is dominant. Hence  $K_2 = (25 \pm 1) \times 10^{-4}$  is immediately found. When  $[\text{I}^-] < 10^{-2}$ ,  $l \simeq K_0 + K_1[\text{I}^-] + K_2[\text{I}^-]^2$  is a very good approximation to eqn. (2) and, as  $K_0$  and  $K_2$  are known, one value of  $K_1$  can be computed from every value of  $l$  determined in this range. For  $K_0$

Table 2. Comparison of the equilibrium constants from the e.m.f. measurements with those from solubility determinations. Temperature 25°C.

Reference	Ref. <sup>8</sup>	This paper	Ref. <sup>9</sup>
Ionic strength	4 M	4 M	2 M
$\text{Ag}_m \text{I}_{m+n}^{n-}$	$k_{m,n}$ (e. m. f.)	$K_n/m$ (sol.)	$K_n/m$ (sol.)
$\text{AgI}_1^-$	—	$(4 \pm 2) \times 10^{-6}$	—
$\text{AgI}_2^{2-}$	$(3 \pm 1) \times 10^{-3}$	$(25 \pm 1) \times 10^{-4}$	$4 \times 10^{-3}$
$\text{AgI}_3^{3-}$	$(9 \pm 1) \times 10^{-3}$	$(11 \pm 1) \times 10^{-3}$	$5 \times 10^{-3}$
$\text{Ag}_2 \text{I}_4^-$	$(10 \pm 6) \times 10^{-4}$	$(15 \pm 5) \times 10^{-4}$	$5 \times 10^{-4}$
$\text{Ag}_3 \text{I}_5^-$	$(23 \pm 5) \times 10^{-4}$	$(20 \pm 3) \times 10^{-4}$	$17 \times 10^{-4}$
$\text{Ag}_4 \text{I}_6^{2-}$	—	$4 \times 10^{-6}$	—

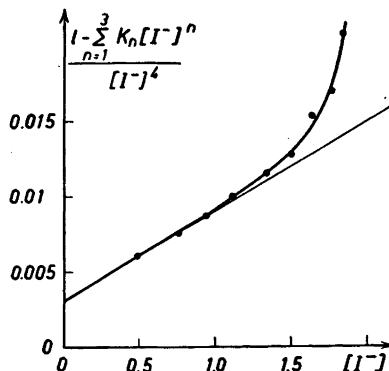


Fig. 2. The computation of  $K_4$  and  $K_5$ .

the value  $5 \times 10^{-9}$  has been used, as this gives a better constancy to  $K_1$  than does the mean value,  $6 \times 10^{-9}$ , from Ref.<sup>8</sup>.  $K_1 = (4 \pm 2) \times 10^{-6}$  is thus obtained. Analogously,  $l \simeq K_2[I^-]^2 + K_3[I^-]^3$  in the range  $0.05 < [I^-] < 0.3$  and hence one value of  $K_3$  can be calculated from every determination of  $l$ ; a mean value,  $K_3 = (11 \pm 1) \times 10^{-4}$ , was found. In all solutions hitherto mentioned the solubility is so small that  $[I^-] \simeq c_{\text{NaI}}$  with sufficient accuracy.

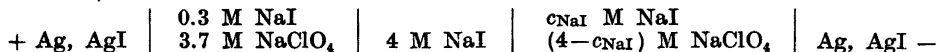
The equilibrium constants  $k_{1,2}$  and  $k_{1,3}$  have been determined recently by e.m.f. measurements (Ref.<sup>9</sup>). These values are compared with the values of  $K_n$  above in Table 2, from which it is evident that  $K_2 = k_{1,2}$  and  $K_3 = k_{1,3}$  within experimental error. Hence it follows that the only significant silver iodide species with the charges  $-2$  and  $-3$  are  $\text{AgI}_3^{2-}$  and  $\text{AgI}_4^{3-}$ .

When the iodide concentrations are greater than 0.3 M, the solutions contain anionic species which have charges larger than 3 and are no longer negligible in quantity. In order to determine the coefficients of the correspond-

ing terms of degree higher than 3 in eqn. (2),  $(l - \sum_{n=1}^3 K_n [I^-]^n) / [I^-]^4$  is plotted

as a function of  $[I^-]$  for numerators  $> 15\%$  of  $l$  (*vide* Fig. 2). As is seen from the graph, this function is very well described by a straight line in the range  $0.5 < [I^-] \leq 1.5$ . The slope of this line gives  $K_5 = (6 \pm 1) \times 10^{-3}$ , and its intersection with the ordinate axis gives  $K_4 = (3 \pm 1) \times 10^{-3}$ . These values have been compared with  $k_{2,5}$  and  $k_{2,4}$  from the e.m.f. measurements in unsaturated solutions (Ref.<sup>9</sup>) in Table 2. It is evident that  $k_{2,4} = \frac{1}{2}K_4$  and  $k_{3,5} = \frac{1}{3}K_5$  within experimental error, as required by eqn. (3) when there is only one species with each charge. As the e.m.f. measurements have been made in a range  $0.003 < c_{\text{Ag}} < 0.1$  corresponding to the range  $0.002 < l < 0.1$ , where the curve in Fig. 2 is with good approximation a straight line, it is evident that the only polynuclear complexes significant at these silver concentrations are  $\text{Ag}_2\text{I}_6^{4-}$  and  $\text{Ag}_3\text{I}_8^{5-}$ , which thus are the only species in the saturated solutions with the charges  $-4$  and  $-5$ .

In this range the solubility is no longer negligible compared with the concentration of sodium iodide. The concentration of free iodide ions had therefore to be determined from the e.m.f. ( $E$  mV) of the following cell:



where the right hand solutions are those listed in Table 1 with  $c_{\text{NaI}} > 0.3$ . The concentration,  $[\text{I}^-]$ , of free iodide in these solutions can be calculated from Nernst's formula

$$E = 59.16 \log \frac{[\text{I}^-]}{0.3} \quad (4)$$

In order to confirm that the results from eqn. (4) are in accordance with the known concentrations of sodium iodide,  $[\text{I}^-]$  was recalculated by inserting the values of  $[\text{I}^-]$  from eqn. (4) in the right hand member of eqn. (5).

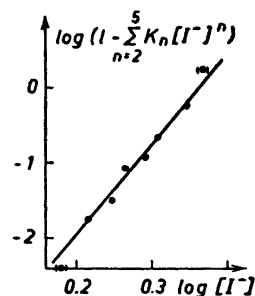
$$[\text{I}^-] = c_{\text{NaI}} - 2K_2[\text{I}^-]^2 - 3K_3[\text{I}^-]^3 - 2K_4[\text{I}^-]^4 - \frac{5}{3}K_5[\text{I}^-]^5 - [\text{P}] \quad (5)$$

The negative terms of this equation represent the concentration of iodide used in the formation (1) of the complexes, if these are  $\text{AgI}_3^{2-}$ ,  $\text{AgI}_4^{3-}$ ,  $\text{Ag}_2\text{I}_6^{4-}$ , and  $\text{Ag}_3\text{I}_9^{5-}$ , as has been found by e.m.f. measurements (Ref.<sup>9</sup> and see above). The term  $-\text{[P]}$ , discussed below, is negligible, when  $[\text{I}^-] < 1.5$ . The results from eqns. (4) and (5) (*vide* Table 1) agree, when the solubility is less than 0.2 M. At higher silver concentrations eqn. (4) gives absurdly high values of  $[\text{I}^-]$ , e. g.  $[\text{I}^-] = 2.83$  for  $c_{\text{NaI}} = 3.85$ , in all probability because of increasing liquid junction potentials and changed activity factors.

At higher iodide concentrations the curve of Fig. 2 becomes increasingly steeper, which means that anionic complexes are formed with charges higher than 5. To analyse this region, it is again necessary to compute values of  $[\text{I}^-]$ , which can no longer be determined by e.m.f. measurements (see above). This computation has been done as follows. It can be deduced (*vide* Ref.<sup>10</sup>) from Erber's<sup>11</sup> determinations of the solubility of silver iodide in highly concentrated solutions of hydrogen iodide that the complexes formed, either have the composition  $\text{Ag}_m\text{I}_{2m}^{m-}$  (with a rather high value of  $m$ , say at least 8), or a composition which comes close to this, e. g.  $\text{Ag}_m\text{I}_{2m+2}^{(m+2)-}$  for large values of  $m$ . Erber himself claimed that the ion  $\text{Ag}_2\text{I}_6^{4-}$  predominates in his concentrated solutions, but he arrived at this false conclusion by assuming that  $c_{\text{NaI}} = [\text{I}^-]$  within the accuracy of his experiments. Erber, however, used this approximation for very high solubilities where it does not hold, e. g. for  $c_{\text{NaI}} \simeq 7$  and  $l \simeq 5$  (hence  $[\text{I}^-] \simeq 2$ , i. e.  $[\text{I}^-]^4 \ll c_{\text{NaI}}^4$ ). Hence it follows that the concentration of free iodide ions must be calculated from eqn. (5), where  $[\text{P}]$  means the concentration of silver, present in complexes with ionic weights larger than that of  $\text{Ag}_3\text{I}_9^{5-}$ . The solubility is described by

$$l = \sum_{n=2}^5 K_n [\text{I}^-]^n + [\text{P}] \quad (6)$$

Fig. 3. The concentration,  $[P] = l - \sum_{n=2}^5 K_n [I^-]^n$ , of silver present in species of ionic weight greater than  $Ag_3I_8^5$ .



in this range. Values of  $[P]$  and  $[I^-]$ , which satisfy both eqn. (5) and eqn. (6) are easily found for each known pair of  $l$  and  $c_{NaI}$ . The resulting values of  $[I^-]$  are given in Table 1. This approach ought to give rather good values of  $[I^-]$ , as, according to Erber's measurements, the highly condensed complexes, dominant when  $[P]$  is large, are either exactly of the form  $Ag_m I_{2m}^{m-}$  or very close to it, which means that the amount of iodide ions used in the formation of these complexes (*vide* reaction (1)) is equal to  $[P]$ , as required by eqn. (5). On the other hand, when  $[P]$  is less, the iodide bound in complex species is presumably a little larger than  $[P]$ , as the complexes are probably of the form  $Ag_m I_{2m+2}^{(m+2)-}$ . Fortunately in this case  $[P]$  is such a small correction term in eqn. (5), that it does not matter that this term ought strictly to be replaced by the slightly greater term  $\frac{m+2}{m} \cdot [P]$ , ( $m \geq 4$ ).

The result of the computation is shown in Fig. 3.  $\log [P]$  is seen to be a rectilinear function of  $\log [I^-]$  with the slope 12 in the whole range, where  $[P]$  is sufficiently large to be calculated from eqn. (6). This connection is approximately valid even for the last solution of Table 1, in spite of the change in ionic strength from 4 M to 6 M.

#### SURVEY OF THE SILVER IODIDE SYSTEM

A. *Uncharged and cationic complexes.* These have been studied by the dissolution of silver iodide in aqueous solutions of silver perchlorate<sup>8</sup>. The complexes are probably of the form  $Ag_n I^{n-1}$  with  $n = 1, 2, 3$ , and 4. At high concentrations of silver perchlorate small amounts of complexes containing more than one iodide ion are probably formed. King, Krall, and Pandow<sup>3</sup> came to the same conclusion, because their measurements of the light absorption at the wave length 300  $m\mu$  showed that Beer's law is not obeyed exactly in solutions of silver perchlorate, undersaturated with silver iodide.

B. *Mononuclear complexes,  $AgI_n^{1-n}$ .* The existence of the species  $AgI_3^{2-}$  and  $AgI_4^{3-}$  has been shown both by e.m.f. measurements and solubility determinations. The two methods gave complexity constants, which were in agreement. The solubility measurements have also given evidence of species of charge 0 and  $-1$ . These species exist in noticeable concentration only when the solubility is small ( $\sim 10^{-8}$  M), which makes it rather probable that these

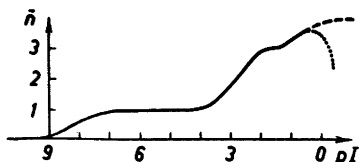


Fig. 4. The formation curves,  $\bar{n}$ , for saturated solutions of AgI (dotted curve) and for solutions containing so little silver, that polynuclear complexes can be neglected (dashed curve). When these two curves coincide they have been full-drawn.

species are mononuclear, *i. e.* of the form  $\text{AgI}$  and  $\text{AgI}_2^-$ . This cannot, however, be established by e.m.f. measurements because of the small total silver concentrations. The formation curve,  $\bar{n}$ , of the mononuclear complexes is shown in Fig. 4. A remarkable feature is the relatively high stability of the first and — to a less extent — of the third complex of the series.

This is in accordance with the idea of a dative  $\pi$ -bond between transition metals with filled d-orbitals and ligands with vacant d-orbitals of suitable size and energy level, as discussed by Chatt<sup>12,13</sup> and Chatt and Wilkins<sup>14</sup>, who also give further literature. That the co-ordination number of silver can sometimes be 3 with strongly bound ligands containing a donor atom with vacant d-orbitals has been shown by Ahrlund and Chatt<sup>15</sup> in their study of some complexes of silver ion with a tertiary phosphine. In the silver iodide case the strength of the first complex,  $\text{AgI}$ , relative to the second,  $\text{AgI}_2^-$ , is even still more pronounced than in the phosphine complexes studied by Ahrlund and Chatt. There is a distinct "stop" in the formation curve of Fig. 4 at  $\bar{n} = 3$ , though the complex formation continues to the 4th complex at high iodide concentrations. This could perhaps mean that the species, written above as  $\text{AgI}_3^{2-}$ , actually has this formula and the possible fourth co-ordination place is not occupied by a molecule of water. This accords with Stroock's<sup>16</sup> study of the high temperature form of solid silver iodide,  $\alpha$ -AgI. Stroock claims that  $\alpha$ -AgI contains as well as two-, three- and four-co-ordinated silver ions in its iodide lattice.

In the silver thiocyanate<sup>7</sup> and azide systems<sup>17</sup> the complex  $\text{AgA}_2^-$  is more stable than the other members of the mononuclear series. From Fig. 4 it is evident that  $\text{AgI}_2^-$  is the least stable intermediate species. It is known<sup>5,6</sup> from the other silver halides that the activity factors at high ionic strength do not favour  $\text{AgA}_2^-$  relative to the other mononuclear species. It seems probable, therefore, that an  $\bar{n}$ -curve for the iodide system at zero ionic strength would show a "stop", *i. e.* a point of inflexion with a low slope of the tangent, at  $\bar{n} = 2$ , too. This means that the equilibrium constants,  $b_{1,n}$ , of the successive steps (Table 3) will differ markedly from the thermodynamic constants. In spite of this, however, the silver iodide system seems to be rather abnormal ( $b_{1,1}/b_{1,2}$  being very great even after a correction for the activity factors) and this might suggest that different types of bonding occur at the different steps.

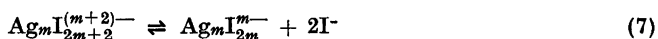
C. *Polynuclear anionic complexes.* The existence of  $\text{Ag}_3\text{I}_3^-$  is conclusively shown by the agreement between the results of the e.m.f. and solubility measurements. There can be little doubt about  $\text{Ag}_2\text{I}_3^{2-}$ , even if the silver present in this species never exceeds 20% of the total silver concentration. It is reasonable to suppose that the two species are formed by the two condensation reactions written at the bottom of Table 3. This would indicate that the silver ion is four-co-ordinated in these species just as it is in the normal solid silver iodide,  $\gamma$ -AgI. The solubility measurements have shown that anionic

Table 3. The step reactions, their equilibrium constants,  $b_{m,n}$ , and their over-all complexity constants,  $\beta_{m,n} = k_{m,n}/K_{-1}$ . Ionic strength 4 M (NaClO<sub>4</sub>). Temperature 25° C.

$\text{Ag}^+ + \text{I}^- \rightleftharpoons \text{AgI}$	$b_{1,1} \approx 10^8$	$\beta_{1,1} \approx 10^8$
$\text{AgI} + \text{I}^- \rightleftharpoons \text{AgI}_2^-$	$b_{1,2} \approx 10^3$	$\beta_{1,2} \approx 10^{11}$
$\text{AgI}_2^- + \text{I}^- \rightleftharpoons \text{AgI}_3^{2-}$	$b_{1,3} \approx 600$	$\beta_{1,3} = (6 \pm 1) \times 10^{13}$
$\text{AgI}_3^{2-} + \text{I}^- \rightleftharpoons \text{AgI}_4^{3-}$	$b_{1,4} \approx 4$	$\beta_{1,4} = (21 \pm 2) \times 10^{13}$
$2 \text{AgI}_4^{3-} \rightleftharpoons \text{Ag}_2\text{I}_6^{4-} + 2 \text{I}^-$	$b_{2,6} \approx 15$	$\beta_{2,6} = (6 \pm 2) \times 10^{29}$
$\text{AgI}_4^{3-} + \text{Ag}_2\text{I}_6^{4-} \rightleftharpoons \text{Ag}_3\text{I}_8^{5-} + 2 \text{I}^-$	$b_{3,8} \approx 250$	$\beta_{3,8} = (24 \pm 2) \times 10^{45}$

complexes are formed with (negative) charges larger than 5. As is shown by Fig. 3 the solubilities can be interpreted assuming that only one such species, *viz.*  $\text{Ag}_{12}\text{I}_{24}^{12-}$ , is formed. It does not prove that this is the only highly condensed species in these concentrated solutions or that this particular species exists at all. It merely shows that  $\text{Ag}_{12}\text{I}_{24}^{12-}$  can be regarded as a summarizing mean of the anionic complexes with high ionic weight. (For criticism of the propensity for selecting rather arbitrary species to describe complex systems, *vide* Hietanen and Sillén<sup>18</sup>, Sillén<sup>19</sup>, or Ahrlund, Hietanen, and Sillén<sup>20</sup>.) In the range where e.m.f. measurements<sup>9</sup> have been carried out, the silver concentration of the complexes, summarized as [P], *i. e.* formally  $12[\text{Ag}_2\text{I}_{24}^{12-}]$ , in Fig. 3, would be quite negligible, in agreement with the fact that no other species than  $\text{Ag}_2\text{I}_6^{4-}$  and  $\text{Ag}_3\text{I}_8^{5-}$  were needed to describe the potentiometric measurements.

An attempt<sup>10</sup> to describe the solubility measurements by assuming an infinite series of complexes,  $\text{Ag}_m\text{I}_{2m+2}^{(m+2)-}$ , formed by condensation reactions, of which all, except the first one, had the same equilibrium constant, accommodated all except the two last determinations of Table 1. E. m. f. measurements in the silver iodide system<sup>9</sup> might also be described by assuming an infinite series of complexes,  $\text{Ag}_m\text{I}_{2m+2}^{(m+2)-}$ , but the equilibrium constants calculated from the e. m. f. s on this assumption did not agree very well with those calculated from the solubility measurements. A quantitative description of the higher condensation products by such an infinite series was therefore abandoned. The most probable hypothesis is that the condensation reactions continue to some rather high value of  $m$  in  $\text{Ag}_m\text{I}_{2m+2}^{(m+2)-}$ , but with increasing charge the reaction with new  $\text{AgI}_2^-$  becomes more difficult. It is also possible that a reaction, *e. g.* a ring-closure,



occurs at some condensation step. It would be very difficult to decide between an infinite series and a series, cut off by a reaction such as (7) with a high value of  $m$ . In the former case the curve  $\log l = f(\log[\text{I}^-])$  would have a vertical asymptote, in the latter one an asymptote with the large slope  $m$ . Perhaps the structure of the species with high ionic weights can be obtained from an X-ray analysis of solutions of silver iodide. A concentrated aqueous solution of lithium iodide, saturated with silver iodide gives X-ray photographs with distinct refraction patterns, which show that the polynuclear complexes are built up by tetrahedral  $\text{AgI}_4^-$ -links (Nilsson<sup>21</sup>). Chains of such links sharing corners have been found in solid  $\text{K}_2\text{AgI}_3$  (Brink and Kroese<sup>22</sup>) and double chains of the same links sharing edges in  $\text{CsAg}_2\text{I}_3$  (Brink, Binnendijk, and van de Linde<sup>23</sup>).

Although it has not been possible to determine the composition of the species, summarized as P above, certain forms can be excluded. They cannot be dinuclear,  $\text{Ag}_2\text{I}_4^{2-}$ — $\text{Ag}_2\text{I}_6^{4-}$ , as Bodländer and Eberlein<sup>24</sup> have claimed, as



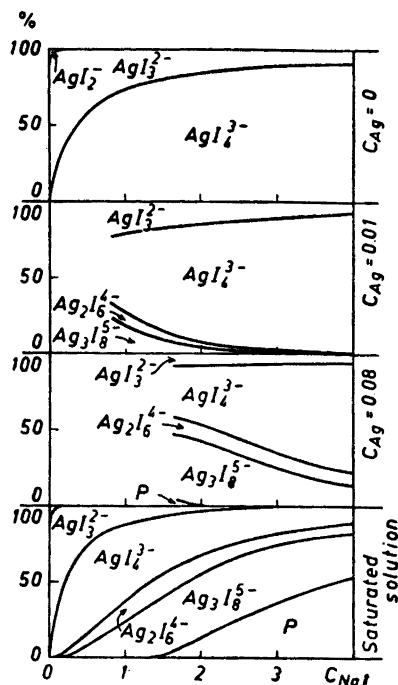


Fig. 5. The distribution of silver in anionic species in saturated solutions, in solutions containing a constant total silver concentration  $c_{Ag} = 0.08$  or  $0.01$  M respectively, and in the limiting case  $c_{Ag} = 0$ .

all species with the charges  $-2$  to  $-5$  have been quantitatively determined both by e.m.f. and solubility measurements. Similarly  $Ag_4I_6^{3-}$ , which Mackor<sup>25</sup> has found in a solvent of acetone and water is excluded. The silver iodide system seems to be completely different in organic solvents because  $AgI_2$  appears to be the limit of mononuclear complex formation both in acetone (Mackor<sup>25</sup>) and in ether (Alin, Evers, and Sillén<sup>26</sup>).

There is an obvious difference between the condensation reactions above and the corresponding "core + link"-description used by Sillén's school in studying hydrolysis of metal ions, as the link is uncharged in those hydrolyses — except in that of thorium — where an infinite series of hydrolysis products is formed. (The hydrolysis of bismuth seems to be under revision, *vide* Hietanen and Sillén<sup>19,p.1622</sup>. Hence the ionic charges of hydrolysis products do not increase with increasing ionic weight (*cf.* Rossotti and Rossotti<sup>27</sup>).

Data relating to the anionic complexes are summarized in Table 3, which contains the most probable values of the equilibrium constants for the stepwise formation of the complexes. Fig. 5 shows the distribution of silver in the different complexes, in saturated as well as in unsaturated solutions containing  $0.08$  or  $0.01$  M silver. In the two latter cases the curves cannot be continued to the left because the point of saturation has been reached. The figure also shows the distribution of silver at such low silver concentrations that polynuclear complexes are not formed. The calculation of the curves and directions for reading the diagrams are described elsewhere<sup>4,7,8</sup>. The distribution

of silver at low iodide concentration can be judged from Fig. 4. An  $\bar{n}$ -curve for saturated solutions for iodide concentrations higher than 0.1 M, drawn in larger scale than that of Fig. 4, is to be seen in Fig. 3 of Ref.<sup>9</sup>. This latter curve would be only slightly changed (and at the highest iodide concentrations only), if an infinite series of complexes were used instead of the description above. The equilibrium constants of the cationic complexes and the distribution of silver among these are given elsewhere<sup>8</sup>.

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