

Electrometric Investigation of Equilibria between Mercury and Halogen Ions

VI. Complexes between Hg^{2+} and Br^- and some Equilibria involving Solid Mercury(I)bromide

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In continuation of the work at this Institute on mercury-halogen equilibria¹⁻⁵ we have undertaken an investigation of the complexes $\text{Hg}^{2+}-\text{Br}^-$.

By analogy with the $\text{Hg}^{2+}-\text{Cl}^-$ complexes it might be expected that in aqueous solution Hg^{2+} and Br^- form the complexes HgBr^+ , HgBr_2 , HgBr_3^- , and HgBr_4^{2-} . Actually, in none of the papers hitherto published on equilibria of $\text{Hg}^{2+}-\text{Br}^-$ complexes, has the existence of all four types of complex been taken into account, and the existing literature data are still more scanty and contradictory than in the case of the chloride complexes.

PREVIOUS WORK

Morse⁶ in 1902 measured the solubility of AgBr in Hg^{2+} solutions. With the assumption that only HgBr^+ was formed, he found $(\text{Hg}^{2+})(\text{Br}^-)(\text{HgBr}^+)^{-1} = \kappa_1^{-1} = 0.4 \cdot 10^{-9}$. (The equilibrium constants κ_1 , κ_2 , κ_3 , κ_4 , q_1 and q_2 have the same meaning as in previous papers in this series; they are moreover listed together with the corresponding reaction formulae in Table 4 of this paper.) From measurements of the solubility of HgBr_2 in $\text{Hg}(\text{NO}_3)_2$ solutions, Morse estimated $(\text{HgBr}^+)^2(\text{Hg}^{2+})^{-1}(\text{HgBr}_2)^{-1} [= k_{12} = \kappa_1^2 \kappa_2^{-1}] = 12$, which value he considered to be rather uncertain. This would give $\kappa_2^{-1} = 2 \cdot 10^{-18}$.

Abegg, Immerwahr (Mrs Haber), and Jander⁷ found in 1902 that Hg_2Br_2 is decomposed by solutions of KBr , metallic mercury being formed and bivalent mercury being dissolved. They explained this phenomenon qualita-

tively by assuming that HgBr₃⁻ was formed, but could not make their results (for 1—3 C KBr) agree quantitatively with the law of mass action. Sherrill⁸, in 1903, showed that this was possible if it was assumed that only HgBr₄²⁻ was formed; he moreover measured the emf of cells with a Hg electrode in a solution containing 1.0 or 2.0 C KBr and 0.88—28.3 mC HgBr₂. From this he concluded $(\text{HgBr}_4^{2-})(\text{Hg}^{2+})^{-1}(\text{Br}^-)^{-4} = \kappa_4 = 4.3 \cdot 10^{21}$.

Sherrill also studied the partition of HgBr₂ between benzene and aqueous solutions of KBr (0.05—0.50 C). On assuming that only HgBr₄²⁻, and no HgBr₃⁻, was formed, he obtained values of $q_2 = (\text{HgBr}_4^{2-})(\text{HgBr}_2)^{-1}(\text{Br}^-)^{-2}$ that varied very widely. He chose the value $q_2 = 2.8 \cdot 10^4$ but concluded that other complexes are formed too. To these he ascribed the general formula $(\text{HgBr}_2)_x(\text{Br}^-)_2$; from freezing and solubility measurements he concluded that x is 2, thus that the principal ionic species besides HgBr₄²⁻ is Hg₂Br₆²⁻.

In 1907, Sand and Breest⁹ showed that Sherrill's analyses could be much better explained if it was assumed that HgBr₃⁻ was the only complex formed. In this case, $q_1 = (\text{HgBr}_3^-)(\text{HgBr}_2)^{-1}(\text{Br}^-)^{-1}$ was found to be rather constant, varying only between 164 and 307 in 12 experiments. By combining κ_4 and q_2 Sherrill had calculated $(\text{Hg}^{2+})(\text{Br}^-)^2(\text{HgBr}_2)^{-1} = \kappa_2^{-1} = q_2 \kappa_4^{-1} = 6.5 \cdot 10^{-18}$; since his q_2 is questionable, this value should not be trusted too much either.

Abegg and Sherrill¹⁰ showed later on that the solubility of Hg₂Br₂ in strong KBr solutions could be explained by means of Sherrill's values of k_s for Hg₂Br₂, κ_2 and q_2 , and the equilibrium constant of Ogg and Abel (quoted by Jonsson *et al.*)³ $k_0 = (\text{Hg}_2^{2+})(\text{Hg}^{2+})^{-1} = 120$. At equilibrium with Hg and Hg₂Br₂, they found $(\text{HgBr}_4^{2-})(\text{Br}^-)^{-2} [= q_2 \kappa_2 k_s k_0^{-1} = \kappa_4 k_s k_0^{-1}] = 0.088$. By combining this value with their values of κ_2 , k_s , and k_0^{-1} , they found $q_2 = 2.9 \cdot 10^4$ in close agreement with the value picked out from Sherrill's partition experiments. These calculations may be a check on their values for κ_4 , k_s and k_0 , and also prove that at the high (Br⁻) employed (1—3 C) the mercury is present chiefly as HgBr₄²⁻. However, since κ_2 was calculated from q_2 and κ_4 , they do not, as Abegg and Sherrill seem to think, give an independent proof of the value of q_2 picked out from the partition experiments at much lower (Br⁻), where, as we now know, the amount of HgBr₃⁻ cannot be neglected.

Since 1903, no measurements of κ_1 or κ_2 for Hg²⁺—Br⁻ has been attempted, as far as we know. There is thus no reliable value of κ_2 , and only one sound determination of κ_1 , that of Morse⁶, giving $\kappa_1 = 2.5 \cdot 10^9$.

The investigators who have applied the law of mass action to equilibria of HgBr₂ with Br⁻ and higher complexes can be divided into two groups: those who neglected the concentration of $(\text{HgBr}_3^-)^{-1}$ and tried to calculate $q_2 = (\text{HgBr}_4^{2-})(\text{HgBr}_2)^{-1}(\text{Br}^-)^{-2}$, and those who calculated $q_1 = (\text{HgBr}_3^-)(\text{HgBr}_2)^{-1}(\text{Br}^-)^{-1}$, neglecting the concentration of HgBr₄²⁻.

The former group consists of Sherrill⁸ ($q_2 = 2.8 \cdot 10^4$, *vide supra*) Job¹¹ (spectrographic method, $q_2^{-1} \approx 1.6 \cdot 10^{-6}$, thus $q_2 \approx 6 \cdot 10^5$ at 16°C) and Fromherz and Lih¹² (spectrographic measurements, $q_2 = 1.4 \cdot 10^4$). In the latter group are Sand and Breest⁹ ($q_1 \approx 200$, *vide supra*) and Garrett¹³, who measured the solubility of HgBr_2 in 0.003—1 m KBr. His results suggest that the HgBr_3^- is the main ion formed with the possibility of only a very small amount of HgBr_4^{2-} ion. On this assumption Garrett found $(\text{HgBr}_3^-) (\text{Br}^-)^{-1} = 1.85$, which in combination with the solubility of HgBr_2 , 0.0170 m, gives $q_1 = 109$.

Of all these measurements, those of Garrett would seem to be the most reliable. However, we shall see that his conclusions are quite at variance with our own.

PLAN OF THE EXPERIMENTS

As in our previous work, the equilibria were studied in solutions of constant acidity ($(\text{H}^+) = 10$ mC) and practically constant ionic strength ($(\text{ClO}_4^-) = 500$ mC or, for $X_e > \text{O}$, $(\text{ClO}_4^-) + X_e = 500$ mC). The apparatus was the same as that described previously.

The equilibrium constant $k_{12} = \kappa_1^2 \kappa_2^{-1} = (\text{HgBr}^+)^2 (\text{Hg}^{2+})^{-1} (\text{HgBr}_2)^{-1}$ has already been measured by Sillén and Infeldt² who found $k_{12} = 5.8 \pm 0.3$.

The determination of κ_1 and κ_2 for $\text{Hg}^{2+} - \text{Br}^-$ was analogous to that for $\text{Hg}^{2+} - \text{Cl}^-$ ⁽⁵⁾. First the solubility product k_s of Hg_2Br_2 was determined by titrations of Hg_2^{2+} with Br^- , using Hg electrodes. Then the maximum redox emf during titrations of Hg_2^{2+} , Hg^{2+} mixtures with Br^- , together with the known k_{12} and k_s , gave κ_1 and κ_2 .

For the chloride complexes, q_1 and q_2 had been calculated from redox titrations of Hg^{2+} , Hg_2^{2+} mixtures with excess of Cl^- . For Br^- , this method proved impracticable. Instead the free concentration of (Hg^{2+}) in $\text{HgBr}_2 - \text{Br}^-$ mixtures was measured by a Hg electrode. These measurements, which offered certain experimental difficulties, gave directly κ_3 and κ_4 , from which q_1 , q_2 , and a number of other constants (Table 4) were obtained.

DETERMINATION OF k_s

A titration of a Hg_2^{2+} solution with Br^- will, as was previously described for Cl^- in Part III, give the two quantities E_{10} and E_{1X} defined by

$$\begin{aligned} -\text{CE} // \text{Hg}_2^{2+} / \text{Hg} + & E = E_{10} + 29.58 \log (\text{Hg}_2^{2+}) & (1 = \text{III}, 1) \\ -\text{CE} // \text{X}^-, \text{Hg}_2\text{X}_2 / \text{Hg} + & E = E_{1X} - 59.16 \log (\text{X}^-) & (2 = \text{III}, 2) \end{aligned}$$

By combining E_{10} and E_{1X} , the solubility product k_s of Hg_2X_2 can be found:

$$E_{1X} - E_{10} = 29.58 \log k_s \quad (3 = \text{III}, 6)$$

By X_e we denote the concentration of halogen in excess over that needed to form Hg₂X₂ and HgX₂. In the first part of the titration curve, X_e is negative, and

$$E_{10} = E - 29.58 \log (\text{Hg}_2^{2+}) = E - 29.58 \log (-\frac{1}{2} X_e) + \delta E \quad (4 = \text{III}, 12)$$

$$\delta E \approx 12.85 k_0^{-1} + 6.42 \kappa_1 k_0^{-1} \sqrt{k_s} (\text{Hg}_2^{2+})^{-\frac{1}{2}} \quad (5 = \text{III}, 13)$$

The term δE is a correction for the amounts of Hg²⁺ and HgX⁺ present in equilibrium. By inserting the values of κ_1 and k_s for Br, given later in this paper, and the previously known $k_0 = 129.2 \pm 1.0$ (III, 18), we find

$$\begin{aligned} \delta E &= 0.10 + 0.040 (\text{Hg}_2^{2+})^{-\frac{1}{2}} \text{ mV} \\ \text{thus } (\text{Hg}_2^{2+}), \delta E/4\text{mC } &0.12 \text{ mV}/1 \text{ mC } 0.14\text{mV}/0.25 \text{ mC } 0.18 \text{ mV} \end{aligned} \quad (6)$$

These values are only insignificantly higher than those calculated from preliminary values and given in Part III. Before any halogen has been added, $\delta E = 0.10$ mV.

After the equivalence point, there should be a correction, $\delta'' E$, for the presence of HgBr₃⁻ and HgBr₄²⁻, since

$$X_e = (X^-) + (\text{HgX}_3^-) + 2(\text{HgX}_4^{2-}) = X(1 + \kappa_3 k_s k_0^{-1} + 2 \kappa_4 k_s k_0^{-1} X) \quad (7 = \text{III}, 21)$$

which, in combination with (2), gives

$$E_{1X} = E + 59.16 \log X = E + 59.16 \log X_e - \delta'' E \quad (8)$$

$$\begin{aligned} \delta'' E &= 59.16 \log (1 + k_s \kappa_3 k_0^{-1} + 2 k_s \kappa_4 k_0^{-1} X) \approx 25.7 k_s \kappa_3 k_0^{-1} + \\ &+ 51.4 k_s \kappa_4 k_0^{-1} X \end{aligned} \quad (9)$$

By inserting the numerical values

$$\delta'' E = 0.006 + 0.0002_1 X \text{ mV} \quad (10)$$

This is negligible in comparison to the experimental errors.

In Table 1 are given the results of a number of titrations for E_{10} and E_{1X} for Br⁻, using concentrations similar to those in Table 3, Part III. The figure $E_{10} - E_{1X}$, which ought to be constant, is seen to vary widely; in the first 10 titrations the average was 362.3 ± 2.3 mV. (Within each titration E_{1X} for different points generally differed only by one or a few 0.1 mV, and

Table 1. Measurements of E_{10} and E_{1X} .

Date	E_{10}	E_{1X}	$E_{10}-E_{1X}$	Electrode
6. 4. 44	434.5	73.4 ± 0.3	361.1	I I I I I A G G G
22. 4. 44	434.4	69.2 ± 0.2	365.2	
17. 6. 44	434.4	73.7 ± 0.3	360.7	
21. 6. 44	434.4	73.5 ± 0.1	360.9	
27. 6. 44	434.4	73.3 ± 0.2	361.1	
28. 6. 44	434.4	72.4 ± 0.1	362.0	
2. 8. 45	434.8	73.0 ± 0.4	361.8	
8. 1. 46	434.4	71.1 ± 0.2	363.3	
11. 1. 46	434.2	70.0 ± 0.1	363.3	
10. 9. 46	434.6	70.7 ± 0.2	363.9	
16. 2. 48	433.6	70.0 ± 0.1	363.6	G G A A G W W
2. 3. 48	434.8	72.4 ± 0.1	362.4	
10. 3. 48	435.2	72.3 ± 0.3	362.9	
21. 4. 48	435.0	72.7 ± 0.3	362.3	
21. 4. 48	434.6	(73.6 ± 0.2)	361.0	
21. 4. 48	435.3	70.8 ± 0.4	364.5	
20. 5. 48	435.3	70.3 ± 0.2	365.0	

only in one case by as much as ± 0.4 mV). In order to avoid possible disturbances from impurities in the reagents or from slow attainment of equilibrium, a new series of titrations was made with new reagents, where the precipitate of Hg_2Br_2 was allowed to stand for at least two days. In these experiments, 7 titrations gave a somewhat higher average value than before. A possible explanation is that in some of the previous experiments the Hg_2Br_2 was in a fine-grained and thus more soluble state. The average of all seven values is 363.1 ± 1.4 . However, we prefer to exclude the value 361.0, which differs widely from all the others, and then obtain:

$$E_{10}-E_{1X} = -29.58 \log k_s = 363.4 \pm 1.1 \text{ mV} \quad (11)$$

$$\log k_s = -12.285 \pm 0.037$$

$$k_s = (5.2 \pm 0.5)10^{-13} \text{ mC}^3 = (5.2 \pm 0.5)10^{-22}\text{C}^3 \quad (12)$$

$$E_{1X}^{\text{st}} = 71.1 \pm 1.1 \text{ mV} \quad (13)$$

The activity product of Hg_2Br_2 has been given by Brodsky and Scherscher¹⁴ as $K_s = 5.50 \cdot 10^{-23}$. From the standard potentials at 25°C Br^- , $\text{Hg}_2\text{Br}_2/\text{Hg}$: 139.7 mV (Larson¹⁵) and $\text{Hg}_2^{2+}/\text{Hg}$: 797.5 ± 1.0 mV (Bray and Hershey¹⁶) we find $K_s = 5.78 \cdot 10^{-23} \text{ m}^3$. A combination of these values

Table 2. Titrations for E_{\max} .

Date	a	59.16 log a	E_{\max}	Corr	$E_{\max}^{\text{st}} - 59.16 \log a$
31. 1. 48	10.00	59.2	603.0	+ 0.8	(544.6)
25. 2. 48	5.00	41.4	591.8	- 0.9	549.5
26. 2. 48	5.00	41.4	594.0	- 0.4	(552.2)
4. 3. 48	5.00	41.4	592.6	- 1.6	549.6
10. 3. 48	5.00	41.4	591.9	- 0.9	549.6
10. 3. 48	5.00	41.4	592.5	- 1.6	549.5
11. 3. 48	10.00	59.2	609.3	- 0.9	549.2
Average					549.5 ± 0.3

with ours would give about 0.1 for the product of the activity factors in our solutions, which seems reasonable and, also agrees well with our results³ for Hg₂Cl₂. Sherrill⁸ found $k_s = 1.27 \cdot 10^{-21} \text{ C}^3$ in a rather indirect way.

TITRATIONS FOR E_{\max}

Just as for Cl⁻, a solution containing Hg²⁺ and Hg₂²⁺ was titrated with Br⁻, and the maximum emf, using a Pt electrode, was observed. In the first experiments each titration was performed within two or three hours. They gave rather wide variations in the quantity $E_{\max} - 59.16 \log a$ ($a =$ total concentration of Hg^{II}) which ought to be constant. Most values were between 547 and 550 mV, but stray values were observed all over the range from 542 to 552 mV.

In later experiments the volume of T to be added to obtain the maximum point could be calculated approximately from the preliminary values. Then only a few points in the neighbourhood of the maximum were studied, and the equilibrium potential was waited for for several days. Out of seven titrations performed in this way (Table 2), five gave values within the limits 549.5 ± 0.3 mV, whereas the other two, which differed by + 2.7 and - 4.9 mV, were disregarded. We thus accepted the value

$$E_{\max} - 59.16 \log a = 549.5 \pm 0.3 \text{ mV} \quad (14)$$

The inaccuracy may, of course, be larger because of systematic errors.

From (IV,6) we find, using the value $k_{12} = 5.8 \pm 0.3$ (Sillén and Infeldt²):

$$549.5 \pm 0.3 = E_{20} + E_{10} - E_{1X} - 59.16 \log (2 + \sqrt{k_{12}}) - 29.58 \log \kappa_2$$

$$= 559.4 \pm 0.2 + 363.4 \pm 1.1 - 38.1 \pm 0.4 - 29.58 \log \kappa_2$$

which leads to

$$\begin{aligned} 29.58 \log \kappa_2 &= 335.2 \pm 1.3 \\ \log \kappa_2 &= 11.332 \pm 0.044 \\ \kappa_2 &= (2.1_5 \pm 0.2)10^{11} \text{ mC}^{-2} = (2.1_5 \pm 0.2)10^{17} \text{ C}^{-2} \end{aligned} \quad (15)$$

By combination with k_{12} we find

$$\begin{aligned} 2 \log \kappa_1 &= \log \kappa_2 + \log k_{12} = 11.332 \pm 0.044 + 0.763 \pm 0.022 = 12.095 \\ &\pm 0.049 \\ \log \kappa_1 &= 6.048 \pm 0.025 \\ \kappa_1 &= (1.12 \pm 0.06)10^6 \text{ mC}^{-1} = (1.12 \pm 0.06)10^9 \text{ C}^{-1} \end{aligned} \quad (16)$$

It thus seems that Morse's determination of κ_1 and Morse's and Sherrill's estimations of κ_2 give about the right order of magnitude.

TITRATIONS FOR κ_3 AND κ_4

We tried at first to determine q_1 and q_2 for Br^- in the same way as with Cl^- , by titrations of Hg(I,II) mixtures with excess halogen, using platinum electrodes. The electrodes proved to be easily polarized so that a valve potentiometer had to be used. Even then it was difficult to obtain reproducible emfs. With two different Pt electrodes in the same solution the emfs often varied by several tens of mV. Later on, when the equilibrium constants were known, it was found that the measured emfs had sometimes been slightly lower but had generally been higher than the calculated equilibrium emfs.

For studying the equilibria involving HgBr_3^- and HgBr_4^{2-} , we had to resort to the same method as had previously been used by Qvarfort and Sillén (Part VII, to be published) for studying the corresponding equilibria with I^- , namely measuring with a Hg electrode the concentration of free Hg^{2+} in solutions containing HgX_2 and X^- .

In these titrations, the concentrations of all molecular species except X^- , HgX_2 , HgX_3^- , and HgX_4^{2-} , could be neglected, thus

$$\begin{aligned} (\text{Hg}^{\text{II}})_{\text{total}} &= a = (\text{HgX}_2) + (\text{HgX}_3^-) + (\text{HgX}_4^{2-}) = (\text{Hg}^{2+}) X^2 (\kappa_2 + \kappa_3 X + \\ &+ \kappa_4 X^2) \end{aligned} \quad (17)$$

$$X_c = (\text{X}^-) + (\text{HgX}_3^-) + 2(\text{HgX}_4^{2-}) = X + (\text{Hg}^{2+})X^3 (\kappa_3 + 2 \kappa_4 X) \quad (18)$$

It is necessary to choose a and the range of X in such a way that Hg_2X_2 will not precipitate. In equilibrium with Hg and Hg_2X_2 , $(\text{HgX}_2) = k_s k_0^{-1} \kappa_2$; $(\text{HgX}_3^-) = k_s k_0^{-1} \kappa_3 X$; $(\text{HgX}_4^{2-}) = k_s k_0^{-1} \kappa_4 X^2$

Table 3. Titrations for κ_3 and κ_4 . Only every third point is given.

S = 0.1 mC Hg²⁺, 406.5 mC Br⁻
 T = 0.1 mC Hg²⁺ (= a)

v ml	X mC	-E mV		-log(Hg ²⁺)		$a(\text{Hg}^{2+})^{-1}X^{-3}\text{mC}^{-3} \cdot 10^{-11}$	
		A	G	A	G	A	G
0	406.8	108.5	108.3	20.469	20.461	4.38	4.29
6	328.1	98.3 ₅	97.7	20.125	20.102	3.79	3.59
12	274.9	89.7	89.1	19.834	19.813	3.28	3.13
18	236.5	82.7	81.8	19.597	19.565	2.99	2.78
24	207.6	76.5	74.9 ₅	19.387	19.334	2.72	2.41
30	184.9	70.6 ₅	69.2	19.189	19.140	2.44	2.18
36	166.7	65.6	64.4 ₅	19.017 ₅	18.979	2.25	2.06
42	151.8	61.1 ₅	59.8	18.867	18.821	2.12	1.91
48	139.9	57.1	54.3	18.730	18.678	1.99	1.76

S = 0.25 mC Hg²⁺, 336.9 mC Br⁻
 T = 0.25 mC Hg²⁺ (= a)

v ml	X mC	-E mV		-log(Hg ²⁺)		$a(\text{Hg}^{2+})^{-1}X^{-3}\text{mC}^{-3} \cdot 10^{-11}$	
		A	G	A	G	A	G
0	336.9	88.9 ₅	88.5	19.807	19.793	4.19	4.06
6	271.7	78.0	77.9	19.438	19.434	3.42	3.38 ₅
12	227.6	69.3	69.1	19.144	19.136	2.95	2.90
18	195.9	61.7	61.7	18.887	18.885	2.49	2.48
24	171.9	55.6	55.8	18.679	18.682 ₅	2.35	2.37
30	153.1	51.1	52.5	18.527	18.542	2.34	2.62

$$\text{thus } a = k_3 k_0^{-1} (\kappa_2 + \kappa_3 X + \kappa_4 X^2) \tag{19}$$

as can be shown from the definitions of the equilibrium constants. Equation (19) defines for every a a certain minimum value of X (or for every X a maximum value of a) beyond which Hg₂X₂ will tend to precipitate.

Preliminary experiments showed that it was necessary to keep a rather low. With the final values κ_2 , κ_3 , and κ_4 we can calculate /X mC, a_{max} mC/ 10 0.0035/50 0.022/100 0.063/200 0.20/.

Table 3 gives the results of two titrations with a = 0.10 mC and two with a = 0.25 mC. At such low a and at the high X used no perceptible error is involved by using X_e instead of X.

In Fig. 1 the function

$$a(\text{Hg}^{2+})^{-1}X^{-3} = \kappa_2 X^{-1} + \kappa_3 + \kappa_4 X \approx \kappa_3 + \kappa_4 X \tag{20}$$

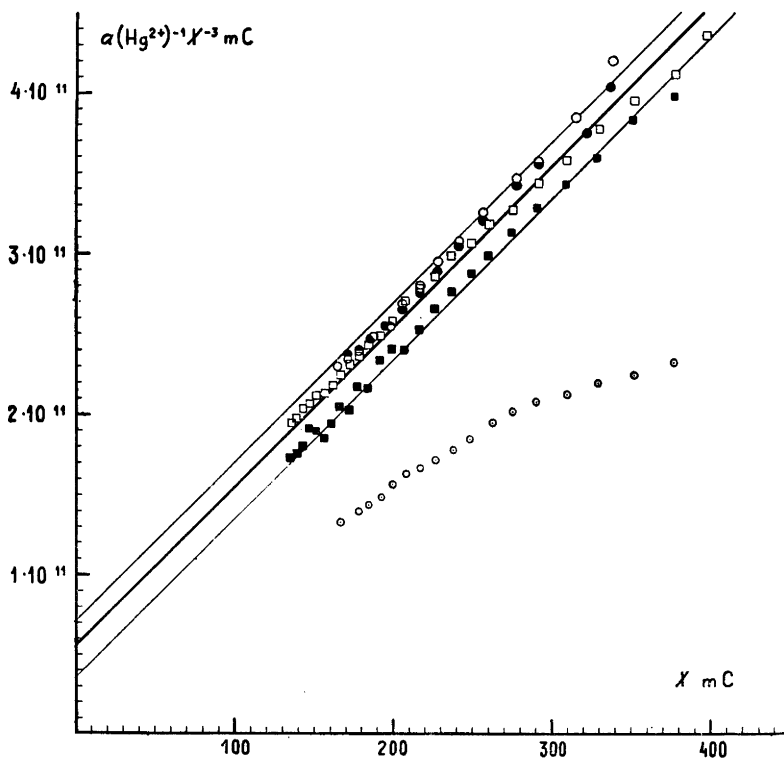


Fig. 1. Titrations for κ_3 and κ_4 . (See Table 3.) Five different titrations. \square Electrode A, $a = 0.1$. \blacksquare Electrode G, $a = 0.1$. \circ Electrode A, $a = 0.25$. \bullet Electrode G, $\sigma = 0.25$. \odot (rejected) A titration where the oxygen was removed from the solution only after mercury had been added.

is plotted against X . The first term, $\kappa_2 X^{-1}$, is negligible in comparison with the others. The points are found to form roughly a straight line; there is no tendency to bending upwards for high X as would be expected if HgX_5^{-3} and higher complexes were to be formed in appreciable amounts.

In these experiments it is very important that air is perfectly excluded, since otherwise quite appreciable quantities of Hg^{II} can be formed by oxidation of the metal. For instance, the lower points in Fig. 1 belong to a rejected titration where the oxygen was removed from the solution only after the electrode mercury had been added with the effect that the actual $(\text{Hg}^{\text{II}})_{\text{tot}}$ was higher than assumed in the calculations. The titrations were broken when Hg_2Br_2 was obtained in the solution. (The present titrations, unlike those in Part VII were performed with decreasing X .) If the titration was performed rather rapidly (a new addition of T every 10 min) the formation of Hg_2Br_2

Table 4. Summary of equilibrium constants.

Reaction	Equilibrium constant	log of equil. const. (C scale)
Hg ²⁺ + Br ⁻ ⇌ HgBr ⁺	$\kappa_1 = \sqrt{k_{12}\kappa_2} = (1.12 \pm 0.06)10^9 C^{-1}$	9.048 ± 0.025
Hg ²⁺ + 2Br ⁻ ⇌ HgBr ₂	$\kappa_2 = (2.15 \pm 0.2)10^{17} C^{-2}$	17.332 ± 0.044
Hg ²⁺ + HgBr ₂ ⇌ 2HgBr ⁺	$k_{12} = 5.8 \pm 0.3$	0.763 ± 0.022
Hg ²⁺ + 3Br ⁻ ⇌ HgBr ₃ ⁻	$\kappa_3 = (0.55 \pm 0.15)10^{20} C^{-3}$	19.740 ± 0.105
Hg ²⁺ + 4Br ⁻ ⇌ HgBr ₄ ²⁻	$\kappa_4 = (1.00 \pm 0.08)10^{21} C^{-4}$	21.000 ± 0.033
HgBr ₂ + Br ⁻ ⇌ HgBr ₃ ⁻	$q_1 = \kappa_3 \kappa_2^{-1} = (260 \pm 70) C^{-1}$	2.408 ± 0.114
HgBr ₂ + 2Br ⁻ ⇌ HgBr ₄ ²⁻	$q_2 = \kappa_4 \kappa_2^{-1} = (4700 \pm 600) C^{-2}$	3.668 ± 0.055
2HgBr ₂ ⇌ HgBr ⁺ + HgBr ₃ ⁻	$\kappa_3 k_{12} \frac{1}{2} \kappa_2^{-\frac{3}{2}} = (1.3 \pm 0.5)10^{-6}$	— 5.880 ± 0.125
2HgBr ₃ ⁻ ⇌ HgBr ₂ + HgBr ₄ ²⁻	$\kappa_2 \kappa_4 \kappa_3^{-2} = 0.07 \pm 0.04$	— 1.148 ± 0.217
Hg ₂ Br ₂ (s) ⇌ Hg ₂ ²⁺ + 2Br ⁻	$k_s = (5.2 \pm 0.5)10^{-22} C^3$	— 21.285 ± 0.037
Hg ₂ Br ₂ + 2Hg ₂ ²⁺ ⇌ Hg ₂ ²⁺ + 2HgBr ⁺	$k_s k_{12} \kappa_2 = (6.45 \pm 1.0)10^{-4} C$	— 3.190 ± 0.062
Hg + Hg ²⁺ ⇌ Hg ₂ ²⁺	$k_0 = 129.2 \pm 1.0$	2.111 ₂ ± 0.003 ₄
Hg ₂ Br ₂ ⇌ Hg + HgBr ₂	$k_s \kappa_2 k_0^{-1} = (8.6 \pm 1.2)10^{-7} C$	— 6.064 ± 0.058
Hg ₂ Br ₂ + Br ⁻ ⇌ Hg + HgBr ₃ ⁻	$k_s \kappa_3 k_0^{-1} = (2.2 \pm 0.7)10^{-4}$	— 3.656 ± 0.111
Hg ₂ Br ₂ + 2Br ⁻ ⇌ Hg + HgBr ₄ ²⁻	$k_s \kappa_4 k_0^{-1} = (4.0 \pm 0.5)10^{-3} C^{-1}$	— 2.396 ± 0.050

was delayed so that measurements could be performed even at lower X than the limit value calculated, as seen from the X values in Table 3. The formation of Hg₂Br₂ was made apparent first by a bend in the $E(v)$ curve, and soon afterwards by an opalescence in the solution.

In Fig. 1, the middle line corresponds to $\kappa_3 = 0.55 \cdot 10^{11}$ (intercept) and $\kappa_4 = 1.00 \cdot 10^9$ (slope). The two thin lines have the same slope but intercepts of $0.35 \cdot 10^{11}$ and $0.70 \cdot 10^{11}$. From the experimental points we concluded the following values for κ_3 and κ_4 :

$$\begin{aligned} \kappa_3 &= (0.55 \pm 0.15)10^{11} \text{ mC}^{-3} = (0.55 \pm 0.15)10^{20} \text{ C}^{-3} \\ \log \kappa_3 &= 10.740 \pm 0.105 \end{aligned} \quad (21)$$

$$\begin{aligned} \kappa_4 &= (1.00 \pm 0.08)10^9 \text{ mC}^{-4} = (1.00 \pm 0.08)10^{21} \text{ C}^{-4} \\ \log \kappa_4 &= 9.000 \pm 0.033 \end{aligned} \quad (22)$$

By combining with κ_2 , we find for q_1 and q_2

$$\begin{aligned} q_1 &= 0.26 \pm 0.07 \text{ mC}^{-1} = 260 \pm 70 \text{ C}^{-1} \\ q_2 &= (4.7 \pm 0.6)10^{-3} \text{ mC}^{-2} = 4700 \pm 600 \text{ C}^{-2} \end{aligned} \quad (23)$$

We can thus see that, contrary to the assumptions made by previous workers, both HgBr_3^- and HgBr_4^{2-} are formed in appreciable amounts.

In Table 4 the equilibrium constants already mentioned are listed together with a few others which can be derived from them.

SUMMARY

By electrometric measurements, a number of equilibrium constants, involving Hg^{2+} , HgBr^+ , HgBr_2 , HgBr_3^- , HgBr_4^{2-} , Hg_2^{2+} , $\text{Hg}_2\text{Br}_2(\text{s})$ and $\text{Hg}(1)$ have been determined. The constants are listed in Table 4. They are valid under the special experimental conditions: 25°C , $(\text{H}^+) = 10\text{ mC}$, ionic strength 500 mC .

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REFERENCES

1. Sillén, L. G. *Svensk Kem. Tid.* **58** (1946) 52 (Part I).
2. Sillén, L. G., and Infeldt, G. *Svensk Kem. Tid.* **58** (1946) 61 (Part II).
3. Jonsson, A., Qvarfort, I., and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 461 (Part III).
4. Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 473 (Part IV).
5. Lindgren, B., Jonsson, A., and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 479 (Part V).
6. Morse, H. *Z. physik. Chem.* **41** (1902) 709.
7. Abegg, R., Immerwahr, C., and Jander, *Z. Elektrochem.* **8** (1902) 688.
8. Sherrill, M. S. *Z. physik. Chem.* **43** (1903) 705.
9. Sand, J., and Breest, F. *Z. physik. Chem.* **59** (1907) 429.
10. Abegg, R., and Sherrill, M. S. *Z. Elektrochem.* **9** (1903) 549.
11. Job, P., *Ann. Chim.* (10) **9** (1928) 162.
12. Fromherz, H., and Lih, K. H. *Z. physik. Chem. A* **167** (1933) 126.
13. Garrett, A. B. *J. Am. Chem. Soc.* **61** (1939) 2744.
14. Brodsky, A. E., and Scherschewer, J. M. *Z. Elektrochem.* **32** (1926) 1; **35** (1929) 836.
15. Larson, W. D. *J. Am. Chem. Soc.* **62** (1940) 765.
16. Bray, W. C., and Hershey, A. V. *J. Am. Chem. Soc.* **56** (1934) 1892.

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