Electrometric Investigation of Equilibria between Mercury and Halogen Ions

VII.* Complexes between Hg²⁺ and I⁻, and some Equilibria involving Solid Mercury(I)Iodide aud Mercury(II)Iodide

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In 1902, Morse [7] measured the solubility of AgI in $Hg(NO_3)_2$ solutions. Assuming that only HgI^+ and no HgI_2 was formed, he calculated with the aid of the solubility product of AgI: $[Hg^{2+}] [I^-] [HgI^+]^{-1} = \varkappa_1^{-1} = 0.4 \cdot 10^{-13}$. From the solubility of HgI_2 in water and in 1 C $Hg(NO_3)_2$ he calculated $[HgI_2][Hg^{2+}] [HgI^+]^{-2} = \varkappa_2\varkappa_1^{-2} = k_{12}^{-1} = 0.016$, and by combining this value, which he considered very inaccurate, with $\varkappa_1$, he obtained $[Hg^{2+}][I^-]^2[HgI_2]^{-1} = \varkappa_2^{-1} = 10^{-25}$.

Sherrill [8], in 1903, measured the emf of cells with a Hg electrode in a solution of HgI_2 and KI, concluded that at the concentrations used (0.04—1.00 C KI, 2.5—305 mC HgI_2) the predominant complex is HgI_4^{2-}, and calculated the equilibrium constant $\varkappa_4 = [HgI_4^{2-}] [Hg^{2+}]^{-1} [I^-]^{-4} = 1.9 \cdot 10^{30}$. According to Frl Hamburger (quoted in [8]), the equilibrium constant for $Hg_2I_2(s) + 2\ I^- \rightleftharpoons Hg(1) + HgI_4^{2-}$ is $[HgI_4^{2-}] [I^-]^{-2} = 2.02$; from this value, in combination with $k_0 = [Hg_2^{2+}] [Hg^{2+}]^{-1} = 120$, and a single value of $\varkappa_4$ (not the average), Sherrill calculated the solubility product for Hg_2I_2 as $[Hg_2^{2+}] [I^-]^2 = 1.2 \cdot 10^{-28}$. He also measured the partition of HgI_2 between benzene and aqueous KI solutions (0.050—1.0 C) and calculated values for $q_2 = [HgI_4^{2-}][HgI_2]^{-1}[I^-]^{-2}$ ranging from $5.9 \cdot 10^5$ to $31 \cdot 10^5$. Of these values for q_2, he considered the most probable to be $q_2 = 7.3 \cdot 10^5$ which together with $\varkappa_4$ gives $\varkappa_2^{-1} = [Hg^{2+}] [I^-]^2 [HgI_2]^{-1} = 3.8 \cdot 10^{-25}$, thus $\varkappa_2 = 2.6 \cdot 10^{24}$. From catalytical measurements of $[I^-]$ in solutions containing 31.25 mC KI and 0—13.15 mC HgI_2 and in solutions with 18—233 mC KI, saturated with HgI_2, he concluded somewhat surprisingly that at these concentrations the predominant complex is $Hg_2I_7^{3-}$. The freezing

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* Part I—VI, see References 1—6.

points of solutions with 0.24—0.74 C KI, saturated with HgI_2, could equally well be interpreted by assuming HgI_4^{2-} and $Hg_2I_7^{3-}$ ions. Abegg and Sherrill [9] have recalculated q_2 by the same vicious circle as for Br^- (c [cf. 6]).

As far as we know, there are no later measurements of the equilibria involving Hg^{2+}, HgI^+, and HgI_2, except those recently made at this Institute. The work on the higher complexes is also scanty and contradictory. By optical methods, Fromherz and Lih [10] found $q_2 = 1.1 \cdot 10^5$, and Job [11] $q_2^{-1} = 1.2 \cdot 10^{-8}$ (at 16° C) thus $q_2 = 0.8 \cdot 10^8$. These three authors considered only HgI_4^{2-}; as did Malyugina et al.[12], who computed $\varkappa_4 = 10^{27}$ from polarographic measurements.

Garrett [13] measured the solubility of HgI_2 in solutions of different $[I^-]$. He could explain his results by assuming both HgI_3^- and HgI_4^{2-} to be present, with the equilibrium constants $[HgI_3^-] [I^-]^{-1} = 0.48$ and $[HgI_4^{2-}] [I^-]^{-2} = 35$. If the solubility of HgI_2 is assumed to be $1.32 \cdot 10^{-4}$ C (the value accepted by Garrett) we can calculate $q_1 = 3600$, $q_2 = 2.7 \cdot 10^5$.

SURVEY

The equilibria between Hg^{2+} and I^- were studied under the same conditions as were chosen for previous investigations of Hg^{2+}—Cl^- and Hg^{2+}—Br^- equilibria; 25° C, $[H^+] = 10$ mC, and ionic strength close to 500 mC, which was achieved by the addition of $NaClO_4$. The apparatus was the same in principle as in earlier work [1-6]. In the latter part of our work, the thermostat was placed in a thermostat room.

However, the methods used for studying the Hg^{2+}—Cl^- and Hg^{2+}—Br^- equilibria could not be taken over unchanged. Thus the equilibria involving HgI_3^- and HgI_4^{2-} (equilibrium constants $\varkappa_3$ and $\varkappa_4$, definition see Table 4) could not be studied by means of redox emfs in solutions containing Hg_2I_2, HgI_3^-, HgI_4^{2-} and I^-; in this case (as later on for the corresponding Br^- equilibria) emfs were measured with a Hg electrode in (HgI_3^-, HgI_4^{2-}, I^-) solutions.

For Hg^{2+}—Cl^- and Hg^{2+}—Br^- the first two complex products, $\varkappa_1$ and $\varkappa_2$, had been obtained by measuring the maximum redox emf during a titration of a Hg^{2+}—Hg_2^{2+} mixture with X^-, and combining this result with the equilibrium constants $k_{12} = [HgX^+]^2 [HgX_2]^{-1} [Hg^{2+}]^{-1}$ measured by Sillén and Infeldt [2]. For I^- this was not possible, since the sparingly soluble HgI_2 precipitated before the desired maximum E had been reached, and since the value for k_{12} was so uncertain in this case that an independent check was necessary. Finally the desired data could be obtained from the redox emf curve using more complicated formulae than for Cl^- and Br^-.

The solubility product k_s of Hg_2I_2 was calculated from titrations of a Hg_2^{2+} solution with I^-, using a Hg electrode. The calculations were analogous to those for Hg_2Cl_2 and Hg_2Br_2, although the corrections for the presence of Hg^{II} complexes were larger than for the other halogens.

The equilibrium constants obtained are listed in Table 4. The equilibria involving Hg^{2+}, the Hg^{2+}—I^- complexes, Hg_2^{2+}, Hg_2I_2, and I^- are analogous to those studied for Cl^- and Br^-. In addition, a few equilibria involving $HgI_2(s)$ are given.

As a by-product we obtained ΔG (25° C) for the reaction $Hg(l) + HgI_2(s) \rightarrow Hg_2I_2(s)$, a figure that should of course be independent of the special composition of the solutions in our experiments.

In the following, the experiments will be recorded in an order different from that followed in the previous parts of this series. The reason is that we have wanted to present straightforward calculations with as little use as possible of constants derived at a later stage.

TITRATIONS FOR $\varkappa_3$ AND $\varkappa_4$

We tried to study the redox potential of solutions of HgI_3^-, HgI_4^{2-} and I^- in equilibrium with solid Hg_2I_2. However, the emf between a Pt electrode in such solutions, and a calomel electrode, proved to be still less reproducible than the corresponding emf with Hg^{II}, $Hg_2Br_2(s)$, and excess of Br^-.

Thus another method had to be used. By means of a Hg electrode we measured the concentration of free Hg^{2+} in a solution containing HgI_3^-, HgI_4^{2-} and I^- (later on analogous measurements were carried out with Br; they were described in Part VI [6]). In such titrations:

$$[Hg^{II}]_{total} = a = [HgX_2] + [HgX_3^-] + [HgX_4^{2-}] = [Hg^{2+}]X^2 \; (\varkappa_2 + \varkappa_3 X + \varkappa_4 X^2)$$
$$(1 = VI, \; 17)$$

$$X_c = [X^-] + [HgX_3^-] + 2 \, [HgX_4^{2-}] = X + [Hg^{2+}]X^3 \; (\varkappa_3 + 2 \, \varkappa_4 X)$$
$$(2 = VI, \; 18)$$

It was necessary to use such concentrations (a and X) that Hg_2X_2 did not precipitate. The condition for equilibrium with Hg and Hg_2X_2:

$$a = [HgX_2] + [HgX_3^-] + [HgX_4^{2-}] = k_s k_0^{-1}(\varkappa_2 + \varkappa_3 X + \varkappa_4 X^2)$$
$$(3 = VI, \; 19)$$

gave when the constants were known for $X = I$, the following maximum values for a: $|X$ mC, a_{max} mC$|1$ $0.014|10$ $0.29|20$ $0.93|50$ $5.03|100$ $19.1|$. Accordingly higher total Hg^{II} concentrations, a, could be used than for Br.

Just as for Br, the concentration of Hg^{2+} was calculated from

$$E^{st} = \tfrac{1}{2} (E_{20} + E_{10}) + 29.58 \log [Hg^{2+}] = 496.95 + 29.58 \log [Hg^{2+}]$$
$$(4 = III, 20)$$

and the function

$$a [Hg^{2+}]^{-1}X^{-3} = \varkappa_2 X^{-1} + \varkappa_3 + \varkappa_4 X \approx \varkappa_3 + \varkappa_4 X \qquad (5 = VI, 20)$$

was computed and plotted against X. Here, too, $[HgX_2]$ can be neglected. As a first approximation we put $X = X_e - 2 a$, and from this first diagram calculated approximate values for $\varkappa_3$ and $\varkappa_4$. Then we calculated the correction

$$X_e - X = [HgX_3^-] + 2 [HgX_4^{2-}] = \frac{a (\varkappa_3 + 2 \varkappa_4 X)}{\varkappa_3 + \varkappa_4 X} = 2 a - a (1 + \varkappa_4 \varkappa_3^{-1} X)^{-1} \quad (6)$$

We used three values for $\varkappa_4 \varkappa_3^{-1}$ (0.1; 0.2 and 0.3 mC^{-1}), one within and one on each side of the range that we thought possible. Formula (6) is easily derived from (2) if $[HgI_2]$ is neglected, which can be shown to be permissible.

In Fig. 1 are plotted the points of (5) for two different titrations for each of the a values 0.5, 2, and 5 mC. Those for 2 mC are recorded in Table 1. The corrections have been made assuming $\varkappa_4 \varkappa_3^{-1}$ to be 0.2 mC^{-1}. (With the other values the differences were insignificant.) From these measurements we estimated

$$\varkappa_3 = (4.0 \pm 1.5) \cdot 10^{18} \text{ mC}^{-3} = (4.0 \pm 1.5) \cdot 10^{27} \text{ C}^{-3}$$
$$\varkappa_4 = (6.8 \pm 0.3) \cdot 10^{17} \text{ mC}^{-4} = (6.8 \pm 0.3) \cdot 10^{29} \text{ C}^{-4} \qquad (7)$$

It seems that Sherrill[8] found the right order of magnitude for $\varkappa_4$ ($1.9 \cdot 10^{30}$), whereas Malyugina's[12] value (10^{27}) was too low. In the literature we have found no direct determination of $\varkappa_3$.

SOLUBILITY OF HgI$_2$

The solubility of HgI$_2$ (s, red) at $25°$ C in a solution containing 490 mC NaClO$_4$, and 10 mC HClO$_4$ has been determined by George Biedermann, mag. chem., using a colorimetric method [14]. He found 0.074 ± 0.003 mC, which value is accepted in our calculations:
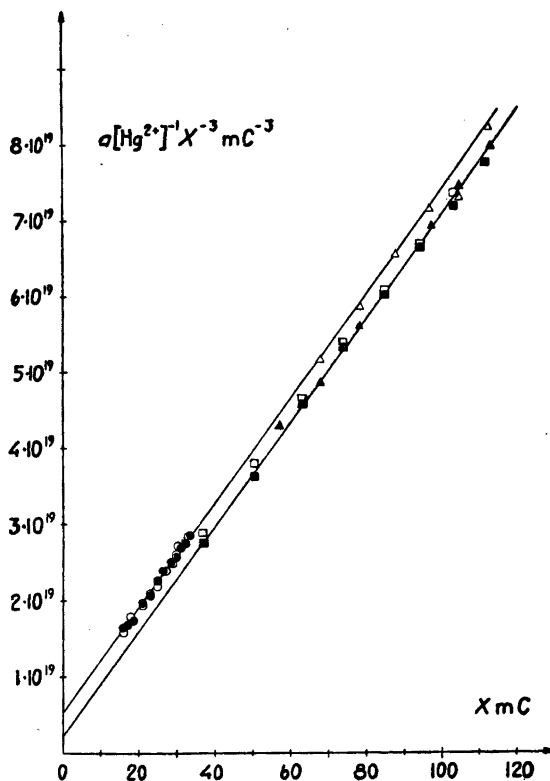
$$s = 0.074 \pm 0.003 \text{ mC} \qquad (8)$$

Fig. 1. *Titrations for* $\varkappa_3$ *and* $\varkappa_4$ *(See Table 1), For* $\bigcirc$ *and* $\bullet$ $a = 0.497_5$ *mC;* $\square$ *and* $\blacksquare$ $a = 1.999$ *mC,* $\triangle$ *and* $\blacktriangle$ $a = 5.049$ *mC. Calomel electrode G was used in all titrations except that marked* $\triangle$, *where A was used. Upper line:* $\varkappa_3 = 5.5 \cdot 10^{18}$ *mC*$^{-3}$; $\varkappa_4 = 6.8 \cdot 10^{17}$ *mC*$^{-4}$. *Lower line:* $\varkappa_3 = 2.5 \cdot 10^{18}$ *mC*$^{-3}$; $\varkappa_4 = 6.8 \cdot 10^{17}$ *mC*$^{-4}$.

TITRATIONS FOR b_1 AND b_2

If Cl^- or Br^- is added to a Hg_2^{2+}—Hg^{2+} solution, the redox potential rises slowly to a maximum value, which is attained at the point where $[HgX^+]$ is maximal, and $[Hg^{2+}] = [HgX_2]$. After this maximum point the redox potential decreases, first slowly and then with increasing slope [4]. From this maximum emf and the value of k_{12} obtained previously [2], we could calculate the values of the first two complex products, $\varkappa_1$ and $\varkappa_2$.

When we tried to make analogous experiments with I^-, however, there was a break in the curve E versus v, the volume of I^- solution added *(cf.* Fig. 2 where the halogen excess X_e is used as coordinate instead of v). The precipitate, which had previously consisted of pure yellow Hg_2I_2, after the break

Table 1. Titrations for $\varkappa_3$ *and* $\varkappa_4$.

Hg electrode, calomel electrode »G»
$S = 1.99_9$ *mC* HgI_2, 9.99_8 *mC* I^- *(100 ml)*
$T = 1.99_9$ *mC* HgI_2, 351.4 *mC* I^- *(v ml)*
■ *4. 9. 1946* □ *6. 9. 1946*

V ml	X_c mC	X mC	$-E$ mV ■	$-E$ mV □	$-\log [Hg^{2+}]$ ■	$-\log [Hg^{2+}]$ □	$a[Hg^{2+}]^{-1}X^{-3}$ mC^{-3} ■	$a[Hg^{2+}]^{-1}X^{-3}$ mC^{-3} □ 10^{-19}
5.00	26.25	22.62	(191.9)	(190.5)	(23.289)	(23.242)	(3.364)	(3.015)
10.00	41.03	37.27	208.6	209.25	23.854	23.876	2.760	2.904
15.00	54.53	50.71	224.2	224.65	24.381	24.396	3.689	3.821
20.00	66.89	63.05	235.4	235.6	24.760	24.766	4.593	4.664
25.00	78.27	74.40	243.7	243.95	25.040	25.049	5.330	5.434
30.00	88.78	84.89	250.4	250.4	25.267	25.267	6.044	6.043
35.00	98.50	94.61	255.8	255.95	25.449	25.454	6.644	6.723
40.00	107.5	103.6	260.35	260.6	25.603	25.612	7.219	7.360
45.00	115.9	112.0	264.35		25.738		7.797	

The values for X were calculated assuming $\varkappa_4\varkappa_3^{-1} = 0.2$ mC^{-1}. For $v = 5$, solid Hg_2I_2 was still present, so the values were not used in our calculations.

also contained red HgI_2. Thus at the concentrations a used by us, the point where $[Hg^{2+}] = [HgI_2]$ could not be attained because of the low solubility of HgI_2. It would have been possible to overcome this by using very low a, but then the attainment of equilibrium could be expected to be slow and the potentials unsteady.

We tried instead to get as much information as possible from the broken curves obtained.

A number of preliminary experiments showed that the attainment of equilibrium was rather slow. Thus, in the titrations which were performed for the calculations and which are represented in Fig. 2, the first point was measured only after 2—5 hours, and the subsequent points each after $\frac{3}{4}$—2 hours' waiting; after these intervals the E seemed to be constant.

For both parts of the curve we have (cf IV, 7), neglecting the concentrations of I^-, HgI_3^-, HgI_4^{2-}, and soluble I^- complexes of Hg_2^{2+},

$$[Hg_2^{2+}]_{\text{total}} = [Hg_2^{2+}] + [Hg_2I_2]_{\text{solid}} \tag{9 a}$$

$$[Hg^{2+}]_{\text{total}} = [Hg^{2+}] + [HgI^+] + [HgI_2] + [HgI_2]_{\text{solid}} = a \tag{9 b}$$

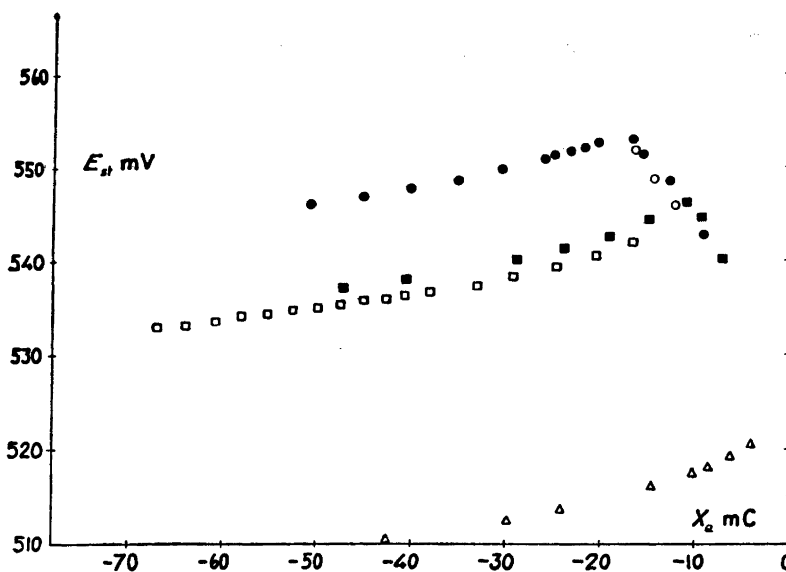$$[I^-]_{\text{total}} = 2[Hg_2I_2]_{\text{solid}} + [HgI^+] + 2[HgI_2] + 2[HgI_2]_{\text{solid}} \tag{9 c}$$

Fig. 2   Titrations for b_1 and b_2, E^{st} (standardized, see [3]) with Pt electrode plotted against X_e.

Symbol	Date	$mC\ Hg^{2+}$	S (100 ml)			T (v ml)	
			$mC\ Hg_2^{2+}$	$mC\ Hg_2I_2$	$mC\ Hg^{2+}$	$mC\ I^-$
△	15. 12. 1947	1.298	20.00	20.01	1.298	100.00
□	1. 12. 1947	3.536	30.00	10.00	3.536	100.00
▣	9. 12. 1947	3.536	20.00	20.01	3.536	100.00
○	29. 7. 1947	5.140	7.78	19.00	5.140	47.40
●	17. 12. 1947	5.181	20.21	10.00	5.181	150.00

The excess of halogen added, X_e (which is negative in these experiments), is defined by

$$X_e = [I^-]_{total} - 2\ [Hg_2^{2+}]_{total} - 2\ [Hg^{2+}]_{total} \qquad (10 = IV,\ 1)$$

It can easily be calculated from known quantities: the volumes added of the solutions S and T, and the concentrations in them of the Hg^{2+}, Hg_2^{2+}, and I^- ions. From (9) and (10)

$$- X_e = 2\ [Hg^{2+}] + [HgI^+] + 2\ [Hg_2^{2+}] \qquad (11 = IV,\ 8)$$
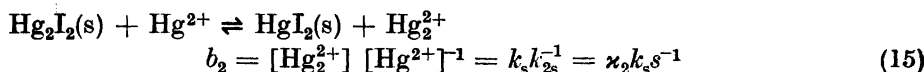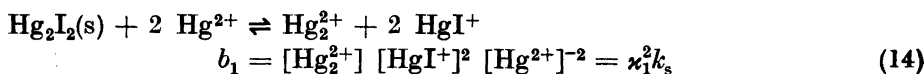
From the emf measured we can calculate directly the ratio

$$q = [Hg^{2+}]^2[Hg_2^{2+}]^{-1} \qquad (12)$$

since $E = E_{20} + 29.58 \log q$ $(13 = \text{III}, 3)$

Thus each titration provides us with a series of corresponding values of X_e and q for the a in question.

We shall find it convenient to introduce the two equilibrium constants:

$$Hg_2I_2(s) + 2 \ Hg^{2+} \rightleftharpoons Hg_2^{2+} + 2 \ HgI^+$$
$$b_1 = [Hg_2^{2+}] \ [HgI^+]^2 \ [Hg^{2+}]^{-2} = \varkappa_1^2 k_s \qquad (14)$$

$$Hg_2I_2(s) + Hg^{2+} \rightleftharpoons HgI_2(s) + Hg_2^{2+}$$
$$b_2 = [Hg_2^{2+}] \ [Hg^{2+}]^{-1} = k_s k_{2s}^{-1} = \varkappa_2 k_s s^{-1} \qquad (15)$$

where k_{2s} is the solubility product of HgI_2:

$$HgI_2(s) \rightleftharpoons Hg^{2+} + 2 \ I^-; \ k_{2s} = [Hg^{2+}] \ [I^-]^2 = s\varkappa_2^{-1} \qquad (16)$$

In the first part of the curve, before HgI_2 has precipitated, only the equilibrium (14) exists, and not (15). If, for brevity's sake, we denote $[Hg^{2+}]$ by x, we find from (12) and (14)

$$[Hg^{2+}] = x; \ [HgI^+] = \sqrt{b_1 q}; \ [Hg_2^{2+}] = x^2 q^{-1} \qquad (17)$$

and from (9 b), (11) and (17), introducing the quantity a'

$$a - [HgI_2] = x + \sqrt{b_1 q} = a' \qquad (18)$$

$$- X_e = 2 \ x + \frac{2 \ x^2}{q} + \sqrt{b_1 q} \qquad (19)$$

From the definitions of the equilibrium constants it is seen that, in equilibrium with solid Hg_2I_2,

$$[HgI_2] = k_s \varkappa_2 \cdot \frac{[Hg^{2+}]}{[Hg_2^{2+}]} = \frac{b_2 s [Hg^{2+}]}{[Hg_2^{2+}]} = \frac{b_2 s q}{x} =$$

$$= \frac{b_2 s q}{a - \sqrt{b_1 q} - [HgI_2]} \qquad (20)$$

Since, in our experiments, $[HgI_2]$ was only a small correction to a, it could be calculated from (20) with all the accuracy needed as soon as approximate values of s, b_1, and b_2 were known.

We eliminate $x = a' - \sqrt{b_1 q}$ from (18) and (19) and find

$$f_1 = b_1 - f_2 \sqrt{b_1} \tag{21}$$

$$f_1 = -\tfrac{1}{2} X_e - a' - a'^2 q^{-1} \tag{22}$$

$$f_2 = \tfrac{1}{2} \sqrt{q} + 2a' q^{-\frac{1}{2}} \tag{23}$$

The calculations were made as follows:

First f_1 and f_2 were calculated by means of (22) and (23) from the known quantities a, X_e, and q neglecting [HgI$_2$], thus using a instead of a'. In a diagram the points $f_1(f_2)$, and a set of lines $y = k - x\sqrt{k}$ (cf. 21) were drawn. The k value corresponding to the points of lowest q (where the correction for HgI$_2$ is negligible) was an approximate value for b_1. Now with this value for b_1 we calculated an approximate value for b_2 in the way to be described below. With these preliminary values for b_1 and b_2 we computed the correction [HgI$_2$] in (18) using (20). Corrected values a' were used for calculating f_1 and f_2, and a new diagram was constructed (Fig. 3). A new approximation was not found necessary and we concluded

$$b_1 = 18.5 \pm 2.5 \text{ mC} \tag{24}$$

For the second part of the curve, after solid HgI$_2$ has appeared, we assume that the equilibria (14) and (15) both exist. From (12), (14) and (15) we find

$$[\text{Hg}^{2+}] = b_2 q; \quad [\text{HgI}^+] = \sqrt{b_1 q}; \quad [\text{Hg}_2^{2+}] = b_2^2 q \tag{25}$$

and thus with (11)

$$- X_e = 2 \ q(b_2 + b_2^2) + \sqrt{b_1 q}$$

or

$$- X_e q^{-\frac{1}{2}} = \sqrt{b_1} + 2(b_2 + b_2^2)\sqrt{q} \tag{26}$$

From (26) it follows that q should be the same function of $(-X_e)$, independent of the original Hg^{II} concentration a. This is fulfilled to a certain extent, as is seen from Fig. 2, where the latter parts of the various curves $E^{st} (X_e)$ almost coincide. The deviations we are inclined to ascribe to the slowness with which solid HgI$_2$ and Hg$_2$I$_2$ attain their stable equilibrium states and to
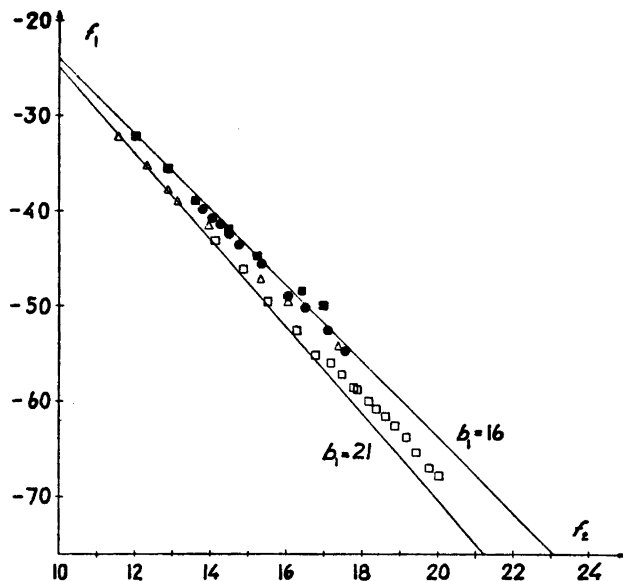
Fig. 3. Diagram for calculating b_1 by means of (21), (22), and (23). The notations for the points from differen ttitrations are the same as in Fig. 2. Upper line: $b_1 = 16$; lower line: $b_1 = 21$. On the addition of more I^- (shift to the right in Fig. 2), f_2 decreases (shift to the upper left in Fig. 3).

the inaccuracy in X_e rather than to the formation of complexes of other types than hitherto assumed, e. g. Hg_2I^{3+} or Hg_2I^+.

In Fig. 4 $(-X_e q^{-\frac{1}{2}})$ has been plotted against $\sqrt{q}$. The points which should according to (26) be situated on a straight line are seen to spread considerably. Thus it is quite impossible from this diagram to compute b_1 and b_2 independently. If, however, the value for b_1 from (24) is accepted, we see that the experimental points all lie between the straight lines corresponding to $b_2 = 2.8$ and $b_2 = 3.28$. We thus conclude

$$b_2 = 3.05 \pm 0.25$$

In these calculations no special weight has been put on the position of the peak in q, since the precipitation of HgI_2 might have been slightly delayed.

Experimental note: The solution S was mixed by adding first the calculated volumes of $NaClO_4$, $HClO_4$, and NaI solutions, then Hg^{2+} solution, and finally Hg_2^{2+}. In this way a yellow precipitate of Hg_2I_2 was obtained, and the emfs were steady. If Hg_2^{2+} was
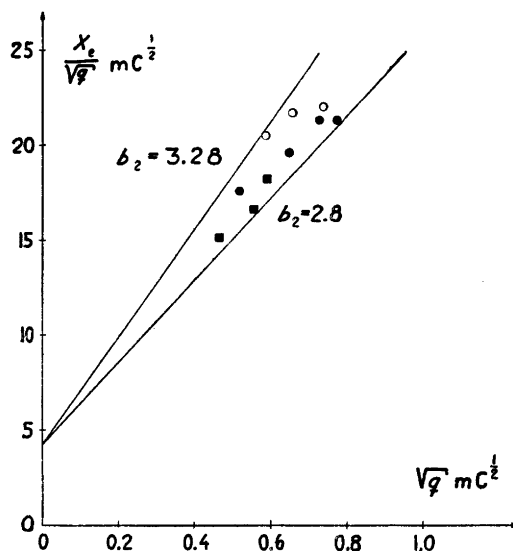
Fig. 4. Diagram for calculating b_2 by means of (26). The notations for the points from different titrations are the same as in Fig. 2. Upper line: $b_1 = 18.5$, $b_2 = 3.28$; lower line: $b_1 = 18.5$, $b_2 = 2.8$.

added before Hg^{2+}, a greenish mixture of Hg_2I_2 and Hg first precipitated, which did not change its colour in a reasonable time, and creeping potentials were obtained.

It was important that all solutions added had already been liberated from air very carefully by nitrogen bubbling before the mixing, since otherwise free iodine appeared.

TITRATIONS FOR k_s

The solubility product k_s of Hg_2I_2 was determined in the same way as for Cl^- and Br^-, by adding I^- to a Hg_2^{2+} solution and measuring E between a Hg electrode in this solution and a calomel electrode with 4 C NaCl. From the first point of the titration, where Hg_2^{2+} is in excess, the quantity E_{10} is calculated by the equation

$$E_{10} = E - 29.58 \log [Hg_2^{2+}] = E - 29.58 \log (-\tfrac{1}{2}X_e) + \delta E \quad (27 = III, 12)$$

where δE is the correction for the amounts of Hg^{2+} and HgX^+ present at equilibrium

$$\delta E \approx 12.85 \ k_0^{-1} + 6.42 \ \varkappa_1 k_0^{-1}\sqrt{k_s}[Hg_2^{2+}]^{-\frac{1}{2}} = 12.85 \ k_0^{-1} + 6.42 \ k_0^{-1}\sqrt{b_1} \ [Hg_2^{2+}]^{-\frac{1}{2}}$$
$$(28 = III, 13)$$

6

By inserting the numerical values for k_o and b_1 with $X^- = I^-$ we find $|[Hg_2^{2+}], \delta E|4$ mC, 0.21 mV|1 mC, 0.31 mV|0.25 mC, 0.53 mV|. Before any I^- has been added, $\delta E = 0.10$ mV as usual. These corrections are practically the same as those calculated from preliminary values in (III, 14).

After the equivalence point there is excess of I^- and

$$X_e = [X^-] + [HgX_3^-] + 2 [HgX_4^{2-}] = X(1 + \varkappa_3 k_s k_0^{-1} + 2 \varkappa_4 k_s k_0^{-1} X)$$
$$(29 = III, 21)$$

The quantity E_{1X} is calculated from

$$E_{1X} = E + 59.16 \log X = E + 59.16 \log X_e - \delta'' E$$
$$\delta'' E \approx 25.7 (\varkappa_3 k_s k_0^{-1} + 2 \varkappa_4 k_s k_0^{-1} X) \qquad (30 = VI, 9)$$

If the numerical values for $X^- = I^-$ are inserted, we find

$$\delta'' E = 0.27 + 0.093 \ X \ \text{mV} \qquad (31)$$

The corrections (28, 31) are thus much larger than for Cl^- and Br^-. However, for the small values of X used by us, the approximations implied in (28) and (31) are still permissible.

Table 2 gives a titration chosen at random, and Table 3 summarizes our measurements of E_{10} and E_{1X} for I^-. As average value we have chosen

$$E_{10} - E_{1X} = -29.58 \log k_s = 546.2 \pm 0.3 \ \text{mV} \qquad (32)$$

Table 2. Titration for E_{1X}.

$S = 4.68$ mC Hg_2^{2+}, 0.045 mC Hg^{2+}
$T = 49.65$ mC I^-

v ml	X_e mC	$59.16 \log X_e$ mV	E mV	$E_{1X} + \delta'' E$ mV	$\delta'' E$ mV	E_{1X} mV
22.80	1.523	10.80	− 123.4	− 112.60	0.41	− 113.01
23.93	1.961	17.31	− 129.75	− 112.44	0.45	− 112.89
24.02	1.995	17.75	− 129.8	− 112.05	0.46	− 112.51
26.24	2.834	26.76	− 138.7	− 111.94	0.53	− 112.47
26.29	2.852	26.92	− 139.0	− 112.08	0.54	− 112.62
29.03	3.845	34.60	− 146.3	− 111.70	0.63	− 112.33
29.07	3.860	34.70	− 146.5	− 111.80	0.63	− 112.43
31.32	4.645	39.46	− 151.2	− 111.74	0.70	− 112.44
33.77	5.469	43.65	− 155.4	− 111.75	0.78	− 112.53
37.16	6.561	48.33	− 160.1	− 111.77	0.88	− 112.65
42.00	8.030	53.52	− 165.2	− 111.68	1.02	− 112.70

Average: $E_{1X} = -112.6$ mV

Table 3. Measurements of E_{10} and E_{1X}.

Month	E_{10}	E_{1X}	$E_{10}-E_{1X}$
7. 1945	434.8	− 111.5	546.3
3. 1946	433.7	− 112.6	546.3
3. 1946	433.8	− 112.4	546.2
11. 1947	433.8	− 112.3	546.1
11. 1947	433.7	− 112.2	545.9
11. 1947	433.75	− 112.7	546.45

Average: 546.2 ± 0.3

thus $\log k_s = -18.465 \pm 0.010$

$$k_s = (3.43 \pm 0.08) \cdot 10^{-19} \text{ mC}^3 = (3.43 \pm 0.08) \cdot 10^{-28} \text{ C}^3 \qquad (33)$$

The activity product of Hg_2I_2 at 25° C has been determined previously by Sherrill [8] ($1.2 \cdot 10^{-28}$) and by Brodsky and Scherschewer [15] ($5.0 \cdot 10^{-29}$). From Bates and Vosburgh's [16] data, Latimer [17] has computed $4.5 \cdot 10^{-29}$. Thus the product of the ionic activity factors in our solutions would be about 0.13 for Hg_2I_2, as compared with about 0.11 for Hg_2Br_2 [6] and 0.09 for Hg_2Cl_2 [5].

DISCUSSION

From the results above we obtain, using (14) and (15),

$$\varkappa_1 = \sqrt{b_1 k_s^{-1}} = (7.3_5 \pm 0.5) \cdot 10^{12} \text{ C}^{-1}$$
$$\varkappa_2 = b_2 s k_s^{-1} = (6.6 \pm 0.6) \cdot 10^{23} \text{ C}^{-2}$$
$$k_{12} = b_1 b_2^{-1} s^{-1} = 82 \pm 14 \qquad (34)$$

Thus Morse [7] and Sherrill [8] found values of the right order of magnitude (Morse $\varkappa_1 = 2.5 \cdot 10^{13}$, $\varkappa_2 \approx 10^{25}$; Sherrill $\varkappa_2 \approx 2.6 \cdot 10^{24}$). The value 115 ± 25 was found for k_{12} by Sillén and Infeldt [2] under conditions identical with ours We consider our value to be more accurate, though the limits of error overlap We can moreover calculate:

$$q_1 = \varkappa_3 \, \varkappa_2^{-1} = \varkappa_3 k_s b_2^{-1} s^{-1} = 6100 \pm 2400 \text{ C}^{-1}$$
$$q_2 = \varkappa_4 \, \varkappa_2^{-1} = \varkappa_4 k_s b_2^{-1} s^{-1} = (1.03 \pm 0.11) \cdot 10^6 \text{ C}^{-2} \qquad (35)$$

Fromherz and Lih's value for q_2, $(1.1 \cdot 10^5)$ [10], is of the same order of magnitude as ours but not Job's $(0.8 \cdot 10^8)$ [11]. A number of equilibrium constants derived from our measurements are listed in Table 4.
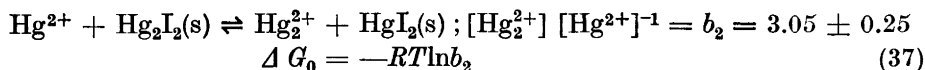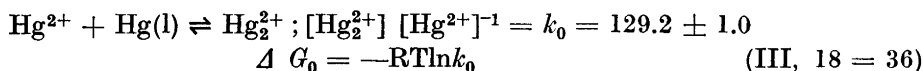
Table 4. Summary of equilibrium constants.

Reaction	Equilibrium constants	log of equil. const. (C scale)
$Hg^{2+} + I^- \rightleftharpoons HgI^+$	$\varkappa_1 = \sqrt{b_1 k_s^{-1}} = (7.3_5 \pm 0.5) \, 10^{12} \, C^{-1}$	12.866 ± 0.028
$Hg^{2+} + 2I^- \rightleftharpoons HgI_2$	$\varkappa_2 = b_2 s k_s^{-1} = (6.6 \pm 0.6) \, 10^{23} \, C^{-2}$	23.818 ± 0.040
$Hg^{2+} + HgI_2 \rightleftharpoons 2HgI^+$	$k_{12} = b_1 b_2^{-1} s^{-1} = 82 \pm 14$	1.914 ± 0.067
$Hg^{2+} + 3I^- \rightleftharpoons HgI_3^-$	$\varkappa_3 = (4.0 \pm 1.5) \, 10^{27} \, C^{-3}$	27.602 ± 0.138
$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	$\varkappa_4 = (6.8 \pm 0.3) \, 10^{29} \, C^{-4}$	29.832 ± 0.019
$HgI_2 + I^- \rightleftharpoons HgI_3^-$	$q_1 = \varkappa_3 k_s b_2^{-1} s^{-1} = 6100 \pm 2400 \, C^{-1}$	3.784 ± 0.144
$HgI_2 + 2I^- \rightleftharpoons HgI_4^{2-}$	$q_2 = \varkappa_4 k_s b_2^{-1} s^{-1} = (1.03 \pm 0.11) \, 10^6 \, C^{-2}$	6.014 ± 0.044
$2HgI_2 \rightleftharpoons HgI^+ + HgI_3^-$	$\varkappa_3 b_1^{\frac{1}{2}} k_s^{\frac{3}{2}} b_2^{-2} s^{-2} = (6.8 \pm 2.8) \, 10^{-8}$	-7.168 ± 0.152
$HgI_2(s) \rightleftharpoons HgI_2$	$s = (7.4 \pm 0.3) \, 10^{-5} \, C$	-4.131 ± 0.018
$HgI_2(s) + I^- \rightleftharpoons HgI_3^-$	$\varkappa_3 k_s b_2^{-1} = 0.45 \pm 0.18$	-0.347 ± 0.143
$HgI_2(s) + 2I^- \rightleftharpoons HgI_4^{2-}$	$\varkappa_4 k_s b_2^{-1} = 76 \pm 8 \, C^{-1}$	1.883 ± 0.040
$Hg_2I_2(s) \rightleftharpoons Hg_2^{2+} + 2I^-$	$k_s = (3.43 \pm 0.08) \, 10^{-28} \, C^3$	-27.465 ± 0.010
$Hg_2I_2(s) + 2Hg^{2+} \rightleftharpoons Hg_2^{2+} + 2HgI^+$	$b_1 = 0.0185 \pm 0.0025 \, C$	-1.733 ± 0.055
$Hg_2I_2(s) + Hg^{2+} \rightleftharpoons HgI_2(s) + Hg_2^{2+}$	$b_2 = 3.05 \pm 0.25$	0.484 ± 0.034
$Hg(l) + Hg^{2+} \rightleftharpoons Hg_2^{2+}$	$k_0 = 129.2 \pm 1.0$	2.111 ± 0.003
$Hg_2I_2(s) \rightleftharpoons Hg(l) + HgI_2$	$s b_2 k_0^{-1} = (1.75 \pm 0.16) \, 10^{-6} \, C$	-5.758 ± 0.039
$Hg_2I_2(s) + I^- \rightleftharpoons Hg(l) + HgI_3^-$	$\varkappa_3 k_s k_0^{-1} = 0.010_6 \pm 0.004$	-1.974 ± 0.138
$Hg_2I_2(s) + 2I^- \rightleftharpoons Hg(l) + HgI_4^{2-}$	$\varkappa_4 k_s k_0^{-1} = 1.80 \pm 0.10 \, C^{-1}$	0.256 ± 0.022

Our equilibrium constants for $HgI_2(s) + I^- \rightleftharpoons HgI_3^-$, and $HgI_2(s) + 2I^- \rightleftharpoons HgI_4^{2-}$; 0.45 ± 0.18, and 76 ± 8, can be compared with Garrett's [13]: 0.48 and 35. Our equilibrium constant for $Hg_2I_2(s) + 2I^- \rightleftharpoons Hg(l) + HgI_4^{2-}$, 1.80 ± 0.10 is not far from Hamburger's [8] value 2.02. It should be remembered that our measurements refer to a constant ionic strength larger than that usually used by these previous workers.

In addition, our measurements permit us to calculate a value for $\varDelta G$ for the reaction between Hg metal, solid HgI_2, and solid Hg_2I_2.

We have studied the two equilibria

$$Hg^{2+} + Hg(l) \rightleftharpoons Hg_2^{2+} \, ; [Hg_2^{2+}] \, [Hg^{2+}]^{-1} = k_0 = 129.2 \pm 1.0$$
$$\varDelta G_0 = -RT \ln k_0 \qquad\qquad (III, 18 = 36)$$

$$Hg^{2+} + Hg_2I_2(s) \rightleftharpoons Hg_2^{2+} + HgI_2(s) \, ; [Hg_2^{2+}] \, [Hg^{2+}]^{-1} = b_2 = 3.05 \pm 0.25$$
$$\varDelta G_0 = -RT \ln b_2 \qquad\qquad (37)$$

Here, $\varDelta G_0$ means $\varDelta G$ for the reaction in question at 25° C with $[Hg_2^{2+}] = 1$ mC, $[Hg^{2+}] = 1$ mC, and the ionic medium used in our experiments. By combination we find

$$Hg(1) + HgI_2(s) \rightarrow Hg_2I_2(s) \ (25°\ C)$$
$$\Delta G = -RT \ln k_0 + RT \ln b_2 = -RT \ln 10 \ (\log k_0 - \log b_2) = -5.708$$
$$(1.627 \pm 0.034) \ kj = -9.29 \pm 0.19 \ kj = -2.22 \pm 0.05 \ kcal \qquad (38)$$
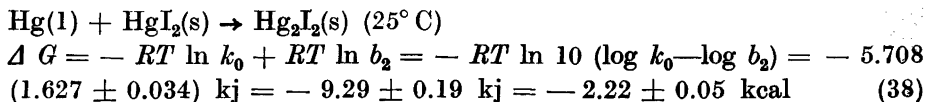
This value should be quite independent of the ionic medium and only influenced by temperature and pressure. Obviously HgI_2 is not stable in the presence of metallic Hg.

SUMMARY

By electrometric measurements, a number of equilibrium constants involving Hg^{2+}, HgI^+, HgI_2, HgI_3^-, HgI_4^{2-}, $HgI_2(s)$, Hg_2^{2+}, $Hg_2I_2(s)$, and $Hg(1)$ have been determined and listed in Table 4. They are valid under the special conditions 25° C, $[H^+] = 10$ mC, ionic strength 500 mC.

For $Hg(1) + HgI_2(s) \rightarrow Hg_2I_2(s)$, ΔG (25° C) $= -9.29 \pm 0.19$ kj $=$
$$= -2.22 \pm 0.05 \ kcal$$
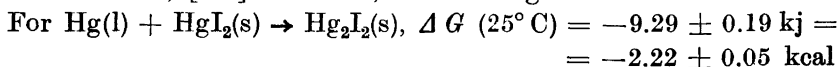
In a concluding paper, the results of this paper and the previous parts I—VI of this series will be discussed and visualized by means of diagrams.

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