Electrometric Investigation of Equilibria between Mercury and Halogen Ions

VII.* Complexes between Hg$^{2+}$ and I$^-$, and some Equilibria involving Solid Mercury(I)Iodide and Mercury(II)Iodide

INGEGERD QVARFORT and LARS GUNNAR SILLÉN

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

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$^{2+}$]$^1$[I$^-$]$^1$[HgI$^+$]$^{-1}$ = $\kappa_1^1 = 0.4 \cdot 10^{-13}$. From the solubility of HgI$_2$ in water and in 1 C Hg(NO$_3$)$_2$ he calculated [HgI$_2$][Hg$^{2+}$][HgI$^+$]$^{-2}$ = $\kappa_2^2 = k_{12}^1 = 0.016$, and by combining this value, which he considered very inaccurate, with $\kappa_1$, he obtained [Hg$^{2+}$][I$^-$]$^2$[HgI$_2$]$^{-1}$ = $\kappa_2^1 = 10^{-25}$.

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 $\kappa_4 = [\text{HgI}_4^{2-}][\text{Hg}^{2+}]^{-1}[\text{I}^-]^{-4} = 1.9 \cdot 10^{30}$. According to FrI Hamburger (quoted in 8), the equilibrium constant for Hg$_2$I$_2$(s) + 2 I$^-$ = Hg(1) + HgI$_4^{2-}$ is [HgI$_4^{2-}$][I$^-$]$^{-2} = 2.02$; from this value, in combination with $k_0 = [\text{Hg}^{2+}][\text{Hg}^{2+}]^{-1} = 120$, and a single value of $\kappa_4$ (not the average), Sherrill calculated the solubility product for Hg$_2$I$_2$ as [Hg$^{2+}$][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 $q_4 = [\text{HgI}_4^{2-}][\text{HgI}_2]^{-1}[\text{I}^-]^{-2}$ ranging from $5.9 \cdot 10^5$ to $31 \cdot 10^5$. Of these values for $q_4$, he considered the most probable to be $q_4 = 7.3 \cdot 10^5$ which together with $\kappa_4$ gives $\kappa_2^1 = [\text{Hg}^{2+}][\text{I}^-]^2[\text{HgI}_2]^{-1}$ = $3.8 \cdot 10^{-28}$, thus $\kappa_2^1 = 2.6 \cdot 10^{34}$. 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$_4$I$_7^2$. The freezing

* Part I—VI, see References 1—6.
points of solutions with 0.24—0.74 C KI, saturated with HgI₂, could equally well be interpreted by assuming HgI₃⁺ and Hg₂I₅⁺ ions. Abegg and Sherrill have recalculated q₂ by the same vicious circle as for Br⁻ (c²⁻, 6).

As far as we know, there are no later measurements of the equilibria involving Hg²⁺, HgI⁺, and HgI₂, except those recently made at this Institute. The work on the higher complexes is also scanty and contradictory. By optical methods, Fromherz and Lih found q₂ = 1.1 · 10⁵, and Job q₂⁻ = 1.2 · 10⁻⁶ (at 16°C) thus q₂ = 0.8 · 10⁸. These three authors considered only HgI₃⁻; as did Malyugina et al., who computed x₄ = 10²⁷ from polarographic measurements.

Garrett measured the solubility of HgI₂ in solutions of different [I⁻]. He could explain his results by assuming both HgI₃ and HgI₄⁻ to be present, with the equilibrium constants [HgI₃][I⁻]⁻¹ = 0.48 and [HgI₄⁻][I⁻]⁻² = 35. If the solubility of HgI₂ is assumed to be 1.32 · 10⁻⁴ C (the value accepted by Garrett) we can calculate q₁ = 3600, q₂ = 2.7 · 10⁴.

SURVEY

The equilibria between Hg²⁺ and I⁻ were studied under the same conditions as were chosen for previous investigations of Hg²⁺—Cl⁻ and Hg²⁺—Br⁻ equilibria; 25°C, [H⁺] = 10 mC, and ionic strength close to 500 mC, which was achieved by the addition of NaClO₄. The apparatus was the same in principle as in earlier work. In the latter part of our work, the thermostat was placed in a thermostat room.

However, the methods used for studying the Hg²⁺—Cl⁻ and Hg²⁺—Br⁻ equilibria could not be taken over unchanged. Thus the equilibria involving HgI₃ and HgI₄⁻ (equilibrium constants x₃ and x₄, definition see Table 4) could not be studied by means of redox emfs in solutions containing Hg₂I₄, HgI₃, HgI₄⁻ and I⁻; in this case (as later on for the corresponding Br⁻ equilibria) emfs were measured with a Hg electrode in (HgI₃, HgI₄⁻, I⁻) solutions.

For Hg²⁺—Cl⁻ and Hg²⁺—Br⁻ the first two complex products, x₁ and x₂, had been obtained by measuring the maximum redox emf during a titration of a Hg²⁺—Hg₂⁺ mixture with X⁻, and combining this result with the equilibrium constants k₁ = [HgX⁺][HgX₂]⁻¹ [Hg²⁺]⁻¹ measured by Sillén and Infeldt. For I⁻ this was not possible, since the sparingly soluble HgI₂ precipitated before the desired maximum E had been reached, and since the value for k₁ 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 \( \text{Hg}_2\text{I}_2 \) was calculated from titrations of a \( \text{Hg}^{2+} \) solution with \( \Gamma^- \), using a Hg electrode. The calculations were analogous to those for \( \text{Hg}_2\text{Cl}_2 \) and \( \text{Hg}_2\text{Br}_2 \), although the corrections for the presence of \( \text{Hg}^{II} \) complexes were larger than for the other halogens.

The equilibrium constants obtained are listed in Table 4. The equilibria involving \( \text{Hg}^{2+} \), the \( \text{Hg}^{2+}—\Gamma^- \) complexes, \( \text{Hg}_2^+ \), \( \text{Hg}_2\text{I}_2 \), and \( \Gamma^- \) are analogous to those studied for \( \text{Cl}^- \) and \( \text{Br}^- \). In addition, a few equilibria involving \( \text{HgI}_2(s) \) are given.

As a by-product we obtained \( \Delta G \) (25° C) for the reaction \( \text{Hg}(l) + \text{HgI}_2(s) \rightarrow \text{HgI}_2(s) \), 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 \( \kappa_3 \) AND \( \kappa_4 \)

We tried to study the redox potential of solutions of \( \text{HgI}_3 \), \( \text{HgI}_4^- \) and \( \Gamma^- \) in equilibrium with solid \( \text{Hg}_2\text{I}_2 \). 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 \( \text{Hg}^{II} \), \( \text{Hg}_2\text{Br}_2(s) \), and excess of \( \text{Br}^- \).

Thus another method had to be used. By means of a Hg electrode we measured the concentration of free \( \text{Hg}^{2+} \) in a solution containing \( \text{HgI}_3 \), \( \text{HgI}_4^- \) and \( \Gamma^- \) (later on analogous measurements were carried out with \( \text{Br}^- \); they were described in Part VI 6). In such titrations:

\[
\begin{align*}
[\text{Hg}^{II}]_{\text{total}} &= a = [\text{HgX}_2] + [\text{HgX}_3] + [\text{HgX}_4^-] = [\text{Hg}^{2+}]X^2 \quad (\kappa_2 + \kappa_3X + \kappa_4X^2) \\
&= a = [\text{HgX}_2] + [\text{HgX}_3] + 2[\text{HgX}_4^-] = X + [\text{Hg}^{2+}]X^3 \quad (\kappa_3 + 2\kappa_4X) \\
&= a = [\text{HgX}_2] + [\text{HgX}_3] + [\text{HgX}_4^-] = k_3k_0^{-1}(\kappa_2 + \kappa_3X + \kappa_4X^2) \\
&= a = [\text{HgX}_2] + [\text{HgX}_3] + [\text{HgX}_4^-] = k_3k_0^{-1}(\kappa_3 + 2\kappa_4X) \\
&= a = [\text{HgX}_2] + [\text{HgX}_3] + [\text{HgX}_4^-] = k_3k_0^{-1}(\kappa_3 + 2\kappa_4X)
\end{align*}
\]

It was necessary to use such concentrations (a and X) that \( \text{Hg}_2\text{X}_4 \) did not precipitate. The condition for equilibrium with Hg and \( \text{Hg}_2\text{X}_4 \):

\[
\begin{align*}
a &= [\text{HgX}_2] + [\text{HgX}_3] + [\text{HgX}_4^-] = k_3k_0^{-1}(\kappa_2 + \kappa_3X + \kappa_4X^2) \\
a &= [\text{HgX}_2] + [\text{HgX}_3] + [\text{HgX}_4^-] = k_3k_0^{-1}(\kappa_3 + 2\kappa_4X) \\
a &= [\text{HgX}_2] + [\text{HgX}_3] + [\text{HgX}_4^-] = k_3k_0^{-1}(\kappa_3 + 2\kappa_4X)
\end{align*}
\]
gave when the constants were known for \( X = I \), the following maximum values for \( a: |X\ mC, a_{\text{max}}\ mC| 10.0.29 \, 10.0.93 \, 50 \, 5.03 \, 100 \, 19.1 \). Accordingly higher total Hg\(^{2+}\) concentrations, \( a \), could be used than for Br.

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

\[
E_{\text{rest}} = \frac{1}{2} (E_0 + E_{10}) + 29.58 \log [\text{Hg}^{2+}] = 496.95 + 29.58 \log [\text{Hg}^{2+}] \quad (4 = \Pi, 20)
\]

and the function

\[
a [\text{Hg}^{2+}]^{-1}X^{-3} = \kappa_2X^{-1} + \kappa_3X + \kappa_4X \approx \kappa_3 + \kappa_4X \quad (5 = \Pi, 20)
\]

was computed and plotted against \( X \). Here, too, \([\text{Hg}X_2]\) can be neglected. As a first approximation we put \( X = X_c = 2a \), and from this first diagram calculated approximate values for \( \kappa_3 \) and \( \kappa_4 \). Then we calculated the correction

\[
X_c - X = [\text{Hg}X_2] + 2 [\text{Hg}X_4]^{-1} = \frac{a (\kappa_2 + 2 \kappa_4X)}{\kappa_2 + \kappa_4X} = 2a - a (1 + \kappa_4X^{-1})^{-1} \quad (6)
\]

We used three values for \( \kappa_4X_3^{-1} \) (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 \([\text{HgI}_2]\) 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 \( \kappa_4X_3^{-1} \) to be 0.2 mC\(^{-1}\). (With the other values the differences were insignificant.) From these measurements we estimated

\[
\kappa_3 = (4.0 \pm 1.5) \cdot 10^{18} \text{ mC}^{-3} = (4.0 \pm 1.5) \cdot 10^{27} \text{ C}^{-3}
\]
\[
\kappa_4 = (6.8 \pm 0.3) \cdot 10^{17} \text{ mC}^{-4} = (6.8 \pm 0.3) \cdot 10^{29} \text{ C}^{-4}
\quad (7)
\]

It seems that Sherrill\(^8\) found the right order of magnitude for \( \kappa_4 (1.9 \cdot 10^{36}) \), whereas Malyugina's\(^{12}\) value \( (10^{27}) \) was too low. In the literature we have found no direct determination of \( \kappa_3 \).

**SOLUBILITY OF HgI\(_2\)**

The solubility of HgI\(_2\) (s, red) at 25\(^\circ\)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:

\[
s = 0.074 \pm 0.003 \text{ mC} \quad (8)
\]
Fig. 1. Titrations for $x_3$ and $x_4$ (See Table 1). For ○ and ● $a = 0.4978 \text{ mc}$; □ and ■ $a = 1.999 \text{ mc}$; Δ and ▲ $a = 5.049 \text{ mc}$. Calomel electrode $G$ was used in all titrations except that marked Δ, where $A$ was used. Upper line: $x_3 = 5.5 \cdot 10^{18} \text{ mc}^{-3}$; $x_4 = 6.8 \cdot 10^{17} \text{ mc}^{-4}$. Lower line: $x_3 = 2.5 \cdot 10^{18} \text{ mc}^{-3}$; $x_4 = 6.8 \cdot 10^{17} \text{ mc}^{-4}$.

TITRATIONS FOR $b_1$ AND $b_2$

If Cl$^-$ or Br$^-$ is added to a Hg$^{2+}$—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, $x_1$ and $x_2$.

When we tried to make analogous experiments with $\Gamma^-$, however, there was a break in the curve $E$ versus $v$, the volume of $\Gamma^-$ 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$_2$I$_2$, after the break
Table 1. Titrations for \( x_3 \) and \( x_4 \).

\[
\begin{array}{cccc|cccc|cccc}
V & X_e & X & E & -\log [\text{Hg}^{2+}] & a [\text{Hg}^{2+}]^{-1} X^{-3} \text{mC}^{-3} \\
\text{ml} & \text{mC} & \text{mC} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV}
\end{array}
\]

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The values for \( X \) were calculated assuming \( x_4 \, x_3^{-1} = 0.2 \text{mC}^{-1} \). For \( v = 5 \), solid \( \text{Hg}_2\text{I}_2 \) was still present, so the values were not used in our calculations.

also contained red \( \text{Hg}_2\text{I}_2 \). Thus at the concentrations \( a \) used by us, the point where \( [\text{Hg}^{2+}] = [\text{Hg}_2\text{I}_2] \) could not be attained because of the low solubility of \( \text{Hg}_2\text{I}_2 \). 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 \( \Gamma^- \), \( \text{Hg}_2\text{I}_3 \), \( \text{Hg}_4\text{I}_4^- \), and soluble \( \Gamma^- \) complexes of \( \text{Hg}_2^{2+} \),

\[
[\text{Hg}_2^{2+}]_{\text{total}} = [\text{Hg}_2^{2+}] + [\text{Hg}_2\text{I}_2]_{\text{solid}}
\]

(9 a)

\[
[\text{Hg}_2^{2+}]_{\text{total}} = [\text{Hg}_2^{2+}] + [\text{HgI}^-] + [\text{HgI}_2] + [\text{HgI}_2]_{\text{solid}} = a
\]

(9 b)

\[
[\Gamma^-]_{\text{total}} = 2 \, [\text{Hg}_2\text{I}_2]_{\text{solid}} + [\text{HgI}^-] + 2 \, [\text{HgI}_2] + 2 \, [\text{HgI}_2]_{\text{solid}}
\]

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

\[
X_e = [\Gamma]_{\text{total}} - 2 [\text{Hg}^{2+}]_{\text{total}} - 2 [\text{Hg}_2^{2+}]_{\text{total}} \quad (10 = \text{IV, 1})
\]

It can easily be calculated from known quantities: the volumes added of the solutions \( S \) and \( T \), and the concentrations in them of the \( \text{Hg}^{2+} \), \( \text{Hg}_2^{2+} \), and \( \Gamma^- \) ions. From (9) and (10)

\[
-X_e = 2 [\text{Hg}^{2+}] + [\text{HgI}^+] + 2 [\text{Hg}_2^{2+}] \quad (11 = \text{IV, 8})
\]

From the emf measured we can calculate directly the ratio

\[
g = [\text{Hg}^{2+}][\text{Hg}_2^{2+}]^{-1} \quad (12)
\]
since \( E = E_2 + 29.58 \log q \quad (13 = \text{III, 3}) \)

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:

\[
\text{Hg}_2\text{I}_2(s) + 2 \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+} + 2 \text{HgI}^+ \\
\quad b_1 = [\text{Hg}_2^{2+}][\text{HgI}^+]^2 [\text{Hg}^{2+}]^{-2} = \chi_1 k_s
\]

(14)

\[
\text{Hg}_2\text{I}_2(s) + \text{Hg}^{2+} \rightleftharpoons \text{HgI}_2(s) + \text{Hg}_2^{2+} \\
\quad b_2 = [\text{Hg}_2^{2+}][\text{Hg}^{2+}]^{-1} = k_s k_{2s}^{-1} = \chi_2 k_s s^{-1}
\]

(15)

where \( k_{2s} \) is the solubility product of \( \text{HgI}_2 \):

\[
\text{HgI}_2(s) \rightleftharpoons \text{Hg}^{2+} + 2 \text{I}^-; \quad k_{2s} = [\text{Hg}^{2+}][\text{I}^-]^2 = s\chi_2^{-1}
\]

(16)

In the first part of the curve, before \( \text{HgI}_2 \) has precipitated, only the equilibrium (14) exists, and not (15). If, for brevity's sake, we denote \([\text{Hg}^{2+}]\) by \( x \), we find from (12) and (14)

\[
[\text{Hg}^{2+}] = x; \quad [\text{HgI}^+] = \sqrt{b_1 q}; \quad [\text{Hg}_2^{2+}] = x^2 q^{-1}
\]

(17)

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

\[
a - [\text{HgI}_2] = x + \sqrt{b_1 q} = a' \\
- X_e = 2 \left( x + \frac{2 x^2}{q} + \sqrt{b_1 q} \right)
\]

(18)

(19)

From the definitions of the equilibrium constants it is seen that, in equilibrium with solid \( \text{Hg}_2\text{I}_2 \),

\[
[\text{HgI}_2] = k_s \chi_2 \cdot \frac{[\text{Hg}^{2+}]}{[\text{Hg}_2^{2+}]} = \frac{b_s [\text{Hg}^{2+}]}{[\text{Hg}_2^{2+}]} = \frac{b_s q}{x}
\]

\[
= \frac{b_s q}{a - \sqrt{b_1 q} - [\text{HgI}_2]}
\]

(20)

Since, in our experiments, \([\text{HgI}_2]\) 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

$$f_1 = b_1 - f_2 \sqrt{b_1}$$  \hspace{1cm} (21)

$$f_1 = -\frac{1}{2} X_e - a' - a'^2 q^{-1}$$  \hspace{1cm} (22)

$$f_2 = \frac{1}{2} V q + 2a' q^{-1}$$  \hspace{1cm} (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 $[\text{HgI}_2]$, 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 $\text{HgI}_2$ 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 $[\text{HgI}_2]$ 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

$$b_1 = 18.5 \pm 2.5 \text{ mC}$$  \hspace{1cm} (24)

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

$$[\text{Hg}^{2+}] = b_2 q; \quad [\text{HgI}^+] = \sqrt{b_1 q}; \quad [\text{Hg}_2^{3+}] = b_2^2 q$$  \hspace{1cm} (25)

and thus with (11)

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

or

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

From (26) it follows that $q$ should be the same function of $(-X_e)$, independent of the original $\text{Hg}^{II}$ concentration $a$. This is fulfilled to a certain extent, as is seen from Fig. 2, where the latter parts of the various curves $E$' (a) almost coincide. The deviations we are inclined to ascribe to the slowness with which solid $\text{HgI}_2$ and $\text{Hg}_2\text{I}_2$ attain their stable equilibrium states and to
the inaccuracy in $X_e$ rather than to the formation of complexes of other types than hitherto assumed, e.g. Hg$_4$I$_{12}^+$ or Hg$_2$I$^+$. In Fig. 4 ($-X_g q^{-1}$) 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 $b_3 = 3.28$. 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$_2$I$^+$. In this way a yellow precipitate of Hg$_4$I$_2$ was obtained, and the emfs were steady. If Hg$_2$I$^+$ was
added before Hg^{2+}, a greenish mixture of Hg\(_2\)I\(_2\) 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\(_2\)I\(_2\) was determined in the same way as for Cl\(^-\) and Br\(^-\), by adding I\(^-\) to a Hg\(_2\)I\(_2\) solution and measuring \( E \) between a Hg electrode in this solution and a calomel electrode with 4 M NaCl. From the first point of the titration, where Hg\(^{2+}\) is in excess, the quantity \( E_{10} \) is calculated by the equation

\[
E_{10} = E - 29.58 \log [\text{Hg}_{2}^{2+}] = E - 29.58 \log (-\frac{1}{2}X_e) + \delta E \quad (27 = \text{III, 12})
\]

where \( \delta E \) is the correction for the amounts of Hg\(^{2+}\) and HgX\(^+\) present at equilibrium.

\[
\delta E \approx 12.85 \ k_0^{-1} + 6.42 \ k_0^{-1} V \frac{k_0 [\text{Hg}_{2}^{2+}]}{[Hg_{2}^{2+}]} \approx 12.85 \ k_0^{-1} + 6.42 \ k_0^{-1} V \frac{b_1 [\text{Hg}_{2}^{2+}]}{[Hg_{2}^{2+}]^1} \quad (28 = \text{III, 13})
\]
By inserting the numerical values for \( k_3 \) and \( b_1 \) with \( X^- = I^- \) we find \([\text{Hg}_2^{2+}]\), \( \delta E | 4 \text{ mC}, 0.21 \text{ mV} | 1 \text{ mC}, 0.31 \text{ mV} | 0.25 \text{ mC}, 0.53 \text{ mV} \). Before any \( I^- \) has been added, \( \delta E = 0.10 \text{ mV} \) 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

\[
X_e = [X^-] + [\text{HgX}_3^-] + 2 [\text{HgX}_4^{2-}] = X(1 + \kappa_3 k_3^{-1} + 2 \kappa_4 k_4^{-1} X) \\
(29 = \text{III, 21})
\]

The quantity \( E_{1X} \) is calculated from

\[
E_{1X} = E + 59.16 \log X = E + 59.16 \log X_e - \delta^* E \\
\delta^* E \approx 25.7 (\kappa_3 k_3^{-1} + 2 \kappa_4 k_4^{-1} X) \\
(30 = \text{VI, 9})
\]

If the numerical values for \( X^- = I^- \) are inserted, we find

\[
\delta^* E = 0.27 + 0.093 X \text{ mV} \\
(31)
\]

The corrections (28, 31) are thus much larger than for \( \text{Cl}^- \) and \( \text{Br}^- \). 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

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

Table 2. Titration for \( E_{1X} \).

\[
\begin{array}{cccccccc}
\text{v} & \text{X_e} & 59.16 \log X_e & E & E_{1X} + \delta^* E & \delta^* E & E_{1X} \\
\text{ml} & \text{mC} & \text{mV} & \text{mV} & \text{mV} & \text{mV} & \text{mV} \\
22.80 & 1.523 & 10.80 & -123.4 & -112.60 & 0.41 & -113.01 \\
23.93 & 1.961 & 17.31 & -129.75 & -112.44 & 0.45 & -112.89 \\
24.02 & 1.995 & 17.75 & -129.8 & -112.05 & 0.46 & -112.51 \\
26.24 & 2.834 & 26.76 & -138.7 & -111.94 & 0.53 & -112.47 \\
26.29 & 2.852 & 26.92 & -139.0 & -112.08 & 0.54 & -112.62 \\
29.03 & 3.845 & 34.60 & -146.3 & -111.70 & 0.63 & -112.33 \\
29.07 & 3.860 & 34.70 & -146.0 & -111.80 & 0.63 & -112.43 \\
31.32 & 4.645 & 39.46 & -151.2 & -111.74 & 0.70 & -112.44 \\
33.77 & 5.469 & 43.65 & -155.4 & -111.75 & 0.78 & -112.53 \\
37.16 & 6.561 & 48.33 & -160.1 & -111.77 & 0.88 & -112.65 \\
42.00 & 8.030 & 53.52 & -165.2 & -111.68 & 1.02 & -112.70 \\
\end{array}
\]

Average: \( E_{1X} = -112.6 \text{ mV} \)
Table 3. Measurements of $E_{10}$ and $E_{1X}$.

<table>
<thead>
<tr>
<th>Month</th>
<th>$E_{10}$</th>
<th>$E_{1X}$</th>
<th>$E_{10} - E_{1X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7. 1945</td>
<td>434.8</td>
<td>111.5</td>
<td>546.3</td>
</tr>
<tr>
<td>3. 1946</td>
<td>432.7</td>
<td>112.6</td>
<td>540.1</td>
</tr>
<tr>
<td>3. 1946</td>
<td>433.8</td>
<td>112.4</td>
<td>541.4</td>
</tr>
<tr>
<td>11. 1947</td>
<td>433.8</td>
<td>112.3</td>
<td>541.5</td>
</tr>
<tr>
<td>11. 1947</td>
<td>433.7</td>
<td>112.2</td>
<td>541.5</td>
</tr>
<tr>
<td>11. 1947</td>
<td>433.75</td>
<td>112.7</td>
<td>541.05</td>
</tr>
</tbody>
</table>

Average: 546.2 ± 0.3

thus log $k_s = -18.465 ± 0.010$

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

The activity product of Hg$_2$I$_2$ at 25°C C has been determined previously by Sherrill $^8$ (1.2 · 10$^{-28}$) and by Brody and Scherschewer $^{15}$ (5.0 · 10$^{-29}$). From Bates and Vosburgh’s $^{16}$ data, Latimer $^{17}$ has computed 4.5 · 10$^{-29}$. Thus the product of the ionic activity factors in our solutions would be about 0.13 for Hg$_2$I$_2$, as compared with about 0.11 for Hg$_2$Br$_2$ $^{(6)}$ and 0.09 for Hg$_2$Cl$_2$ $^{(6)}$.

**DISCUSSION**

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

$$x_1 = \sqrt{b_1 k_s^{-1}} = (7.35 ± 0.5) \cdot 10^{12} \text{ C}^{-1}$$

$$x_2 = b_2^2 k_s^{-1} = (6.6 ± 0.6) \cdot 10^{23} \text{ C}^{-2}$$

$$k_{12} = b_1 b_2^{-1} s^{-1} = 82 ± 14 \quad (34)$$

Thus Morse $^7$ and Sherrill $^8$ found values of the right order of magnitude (Morse $x_1 = 2.5 \cdot 10^{23}$, $x_2 = 10^{25}$; Sherrill $x_2 ≈ 2.6 \cdot 10^{24}$). The value 115 ± 25 was found for $k_{12}$ by Sillén and Infeld $^2$ under conditions identical with ours. We consider our value to be more accurate, though the limits of error overlap.

We can moreover calculate:

$$q_1 = x_2 k_s^{-1} = x_3 k_s k_s^{-1} s^{-1} = 6100 ± 2400 \text{ C}^{-1}$$

$$q_2 = x_4 x_2^{-1} = x_4 k_s b_2^{-1} s^{-1} = (1.03 ± 0.11) \cdot 10^6 \text{ C}^{-2} \quad (35)$$

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constants</th>
<th>log of equil. const. (C scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Hg}^{2+} + \Gamma^{-} \rightleftharpoons \text{HgI}^{+}$</td>
<td>$x_1 = \sqrt{b_1 k_2^{-1}} = (7.3 \pm 0.5) \times 10^{12} \ C^{-1}$</td>
<td>12.866 ± 0.028</td>
</tr>
<tr>
<td>$\text{Hg}^{2+} + 2\Gamma^{-} \rightleftharpoons \text{HgI}_2$</td>
<td>$x_2 = b_2 k_1^{-1} = (6.6 \pm 0.6) \times 10^{22} \ C^{-2}$</td>
<td>23.818 ± 0.040</td>
</tr>
<tr>
<td>$\text{Hg}^{2+} + \text{HgI}_2 \rightleftharpoons 2\text{HgI}^{+}$</td>
<td>$k_{12} = b_1 b_2^{-1} s^{-1} = 82 \pm 14$</td>
<td>1.914 ± 0.067</td>
</tr>
<tr>
<td>$\text{Hg}^{2+} + 3\Gamma^{-} \rightleftharpoons \text{HgI}_3$</td>
<td>$x_3 = (4.0 \pm 1.5) \times 10^{27} \ C^{-3}$</td>
<td>27.602 ± 0.138</td>
</tr>
<tr>
<td>$\text{Hg}^{2+} + 4\Gamma^{-} \rightleftharpoons \text{HgI}_4^{-}$</td>
<td>$x_4 = (6.8 \pm 0.3) \times 10^{29} \ C^{-4}$</td>
<td>29.832 ± 0.019</td>
</tr>
<tr>
<td>$\text{HgI}_2 + \Gamma^{-} \rightleftharpoons \text{HgI}_3^{-}$</td>
<td>$q_1 = x_4 k_3 k_2^{-1} s^{-1} = 6100 \pm 2400 \ C^{-1}$</td>
<td>3.784 ± 0.144</td>
</tr>
<tr>
<td>$\text{HgI}_2 + 2\Gamma^{-} \rightleftharpoons \text{HgI}_4^{-}$</td>
<td>$q_2 = x_4 k_3 k_2^{-1} s^{-1} = (1.03 \pm 0.11) \times 10^6 \ C^{-2}$</td>
<td>6.014 ± 0.044</td>
</tr>
<tr>
<td>$2\text{HgI}_2 \rightleftharpoons \text{HgI}^{+} + \text{HgI}_3^{-}$</td>
<td>$x_2^{1/2} k_1^{1/2} s^{-2} = (6.8 \pm 2.8) \times 10^{-8}$</td>
<td>-7.168 ± 0.152</td>
</tr>
<tr>
<td>$\text{HgI}_2(s) \rightleftharpoons \text{HgI}_2$</td>
<td>$s = (7.4 \pm 0.3) \times 10^{-5} \ C$</td>
<td>-4.131 ± 0.018</td>
</tr>
<tr>
<td>$\text{HgI}_2(s) + \Gamma^{-} \rightleftharpoons \text{HgI}_3^{-}$</td>
<td>$x_4 k_3 k_2^{-1} = 0.45 \pm 0.18$</td>
<td>-0.347 ± 0.143</td>
</tr>
<tr>
<td>$\text{HgI}_2(s) + 2\Gamma^{-} \rightleftharpoons \text{HgI}_4^{-}$</td>
<td>$x_4 k_3 k_2^{-1} = 76 \pm 8 \ C^{-1}$</td>
<td>1.883 ± 0.040</td>
</tr>
<tr>
<td>$\text{HgI}_4^{-}(s) \rightleftharpoons \text{Hg}^{2+} + 2\Gamma^{-}$</td>
<td>$k_1 = (3.43 \pm 0.08) \times 10^{-28} \ C^2$</td>
<td>-27.465 ± 0.010</td>
</tr>
<tr>
<td>$\text{HgI}_4^{-}(s) + 2\text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+} + \text{HgI}_4^{-}$</td>
<td>$b_1 = 0.0185 \pm 0.0025 \ C$</td>
<td>-1.733 ± 0.055</td>
</tr>
<tr>
<td>$\text{HgI}_4^{-}(s) + \text{Hg}^{2+} \rightleftharpoons \text{HgI}_3^{-} + \text{Hg}_2^{2+}$</td>
<td>$b_2 = 3.05 \pm 0.25$</td>
<td>0.484 ± 0.034</td>
</tr>
<tr>
<td>$\text{Hg}(l) + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$</td>
<td>$k_0 = 129.2 \pm 1.0$</td>
<td>2.111 ± 0.003</td>
</tr>
<tr>
<td>$\text{HgI}_2(s) \rightleftharpoons \text{Hg}(l) + \text{HgI}_2$</td>
<td>$s b_2 k_0^{-1} = (1.75 \pm 0.16) \times 10^{-6} \ C$</td>
<td>-5.758 ± 0.039</td>
</tr>
<tr>
<td>$\text{HgI}_2(s) + \Gamma^{-} \rightleftharpoons \text{Hg}(l) + \text{HgI}_3^{-}$</td>
<td>$x_4 k_3 k_0^{-1} = 0.010 \pm 0.004$</td>
<td>-1.974 ± 0.138</td>
</tr>
<tr>
<td>$\text{HgI}_2(s) + 2\Gamma^{-} \rightleftharpoons \text{Hg}(l) + \text{HgI}_4^{-}$</td>
<td>$x_4 k_3 k_0^{-1} = 1.80 \pm 0.10 \ C^{-1}$</td>
<td>0.256 ± 0.022</td>
</tr>
</tbody>
</table>

Our equilibrium constants for $\text{HgI}_2(s) + \Gamma^{-} \rightleftharpoons \text{HgI}_3^{-}$, and $\text{HgI}_2(s) + 2\Gamma^{-} \rightleftharpoons \text{HgI}_4^{-}$; 0.45 ± 0.18, and 76 ± 8, can be compared with Garrett's\textsuperscript{13}: 0.48 and 35. Our equilibrium constant for $\text{HgI}_4^{-}(s) + 2\Gamma^{-} \rightleftharpoons \text{Hg}(l) + \text{HgI}_4^{-}$, 1.80 ± 0.10 is not far from Hamburger's\textsuperscript{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 $\Delta G$ for the reaction between Hg metal, solid $\text{HgI}_2$, and solid $\text{Hg}_2I_2$.

We have studied the two equilibria

$$\text{Hg}^{2+} + \text{Hg}(l) \rightleftharpoons \text{Hg}_2^{2+} ; [\text{Hg}_2^{2+}]^{-1} = k_0 = 129.2 \pm 1.0$$

$$\Delta G_0 = -RT \ln k_0$$

(III, 18 = 36)

$$\text{Hg}^{2+} + \text{HgI}_2(s) \rightleftharpoons \text{Hg}_2^{2+} + \text{HgI}_2(s) ; [\text{Hg}_2^{2+}]^{-1} = b_2 = 3.05 \pm 0.25$$

$$\Delta G_0 = -RT \ln b_2$$

(37)

Here, $\Delta G_0$ means $\Delta G$ for the reaction in question at 25° C with $[\text{Hg}_2^{2+}] = 1$ mC, $[\text{Hg}^{2+}] = 1$ mC, and the ionic medium used in our experiments. By combination we find
Hg(l) + HgI₂(s) → Hg₂I₄(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 ± 0.034) kj = -9.29 ± 0.19 kj = -2.22 ± 0.05 kcal (38)

This value should be quite independent of the ionic medium and only influenced by temperature and pressure. Obviously HgI₂ is not stable in the presence of metallic Hg.

SUMMARY

By electrometric measurements, a number of equilibrium constants involving Hg²⁺, HgI⁺, HgI₂, HgI₃, HgI₅⁺, HgI₆⁺, HgI₄⁺, HgI₅⁺, HgI₆⁺, and Hg(l) 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(l) + HgI₂(s) → Hg₂I₄(s), \( \Delta G \) (25°C) = -9.29 ± 0.19 kj = -2.22 ± 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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