Electrometric Investigation of Equilibria between Mercury and Halogen Ions

III.   The „Millimolar" Potentials of Mercury and the Solubility Product of Mercury (I) Chloride

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In Part I[1] of this series the »millimolar potentials» E_{10}, E_{1X}, and E_{20} were defined as the emf of the cells

$$-CE/ /Hg_2^{2+}/Hg + \qquad E = E_{10} + 29.58 \log (Hg_2^{2+}) \qquad (1)$$

$$-CE/ /X^-, Hg_2X_2/Hg + \qquad E = E_{1X} - 59.16 \log (X^-) \qquad (2)$$

$$-CE/ /Hg_2^{2+}, Hg^{2+}/Pt + \qquad E = E_{20} + 59.16 \log (Hg^{2+}) -$$
$$- 29.58 \log (Hg_2^{2+}) \qquad (3)$$

when all concentrations appearing in the expression for E are 1 mC *. These millimolar potentials are defined under the special experimental conditions we have chosen: at a temperature of 25° C with $(H^+) = 10$ mC and (ClO_4^-) $+ X_{total} = 500$ mC in the right electrode vessel, and with the reference electrode

$$CE = Hg, Hg_2Cl_2/4 \ C \ NaCl/0.5 \ C \ NaClO_4/ \qquad (4)$$

to the left.

The millimolar emf:s are connected with the equilibrium constant for

$$Hg + Hg^{2+} = Hg_2^{2+} \qquad k_0 = (Hg_2^{2+}) (Hg^{2+})^{-1}$$

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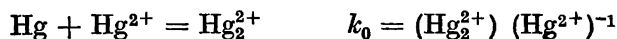
*) C = mole/l; mC = mmole/l.

by the relation

$$E_{20} - E_{10} = 59.16 \log k_0 \qquad (5)$$

The solubility products of the Hg_2X_2 can be calculated from E_{10} and E_{1x} by

$$E_{1x} - E_{10} = 29.58 \log k_s \,; k_s = (Hg_2^{2+}) \, (X^-)^2 \qquad (6)$$

A knowledge of these quantities was necessary for the following calculations on Hg^{2+}—X^- complexes. Now, the four calomel electrodes used — »A», »F», »G» and »I» — had slightly different potentials, as was found for example by direct comparison, connecting them all to a vessel with 4 C NaCl. Moreover these differences varied slightly with time. Accordingly, the values of E_{10} and E_{20} also varied slightly.

In order to make measurements at different times and with different CE:s comparable, we »standardized» all emf:s relative to E_{10}, which was measured every now and then. Where it was necessary a correction was introduced — generally different for the different CE:s — so as to make E_{10} equal to $E_{10}^{st} = 434.5$ mV. These corrections never exceeded 2 mV.

TITRATIONS FOR DETERMINING THE REDOX POTENTIAL E_{20}

To determine E_{20}, titrations were made with Pt electrodes, where S (the original solution in the titration vessel) contained Hg_2^{2+} and T (the solution added during the titration) contained Hg^{2+}. Generally T contained Hg_2^{2+} too in the same concentration as in S, which facilitated the calculation. The first point of such a titration, corresponding to the »pure Hg_2^{2+}» solution, is rather well defined (within 1 or 2 mV) as there is always a certain amount of Hg^{2+} left in a solution prepared by shaking to equilibrium with metallic Hg.

E_{20} and the Hg^{2+} correction could be calculated in two ways:

1) An approximate value of E_{20} was obtained from a point with high (Hg^{2+}); with this E_{20}, the (Hg^{2+}) in the »Hg_2^{2+}» solution was calculated. Then a better value of E_{20} was calculated, and so on.

2) They could also be found by direct calculation. We assume that S contains $(b - \frac{\delta}{2})$ mC Hg_2^{2+} and δ mC Hg^{2+}, and that T contains $(b - \frac{\delta}{2})$ mC Hg_2^{2+} and $(a + \delta)$ mC Hg^{2+}, where a and b are known from the analyses of total Hg content. After addition of v ml of T to 100 ml of S

$$(Hg_2^{2+}) = b - \frac{\delta}{2}, \ (Hg^{2+}) = \delta + av \, (100 + v)^{-1}$$

and according to (3)

$$E(v) = E_{20} + 59.16 \ \log \ [\delta + av \ (100 + v)^{-1}] - 29.58 \ \log \ (b - \tfrac{\delta}{2})$$

$$E(0) = E_{20} + 59.16 \ \log \delta - 29.58 \ \log \ (b - \tfrac{\delta}{2})$$

$$\varDelta E = E(v) - E(0) = 59.16 \ \log \ [1 + av\delta^{-1} \ (100 + v)^{-1}] \tag{7}$$

δ is obtained directly from (7)

The ratio $(Hg_2^{2+})/(Hg^{2+})$ was usually about 100—120 in our »Hg_2^{2+}» solutions, which is not far from the equilibrium constant k_0 obtained by us (see (18)). It cannot be expected to agree exactly, as the equilibrium was established under very different conditions.

Table 1 gives a typical titration for E_{20}, showing the validity of (3).

Table 1. Titration for E_{20}. Pt electrode, CE »G».
$S = (4.863 - \tfrac{\delta}{2}) \ Hg_2^{2+}, \ \delta Hg^{2+}.$
$T = (4.863 - \tfrac{\delta}{2}) \ Hg_2^{2+}, \ (19.47 + \delta) \ Hg^{+2}.$

v ml	E mV	δ mC	(Hg^{2+}) mC	E_{20} mV
0	458.65		0.0437	
5.00	537.8	0.0446	0.971	(558.8_2)
9.97	554.2	0.0439	1.809	559.2_3
15.00	563.45	0.0439	2.583	559.3_3
20.00	569.7	0.0437	3.289	559.3_7
25.00	574.3	0.0437	3.937	559.3_4
30.00	578.0	0.0436	4.537	559.4_0
35.00	580.95	0.0437	5.092	559.3_9
40.03	583.4	0.0437	5.160	559.3_5

When v ml of T had been added the emf was E mV. From $E(0)$ and $E(v)$, δ was calculated by means of formula (7). If an average value $\delta = 0.0437$ mC is accepted, (Hg_2^{2+}) was 4.841 during the entire titration, whereas the calculated values of (Hg^{2+}) are given in the fourth column. Finally E_{20} was calculated by means of (3). The mean value (excluding the value at 5.00 ml where a small error in v causes a large error in E_{20}) was $E_{20} = 559.3_4 \pm 0.1$ mV (not standardized).

THE MERCURY ELECTRODE IN Hg_2^{2+} — Hg^{2+} SOLUTIONS

When a Hg electrode and a solution containing Hg_2^{2+} and Hg^{2+} are in equilibrium in accordance with (4), E can equally well be expressed by (1) or by (3), as in this case the Hg can also be regarded as a redox electrode. One might of course also use the expression for a Hg^{2+}/Hg electrode, which is easily derived from (1) and (3):

$$— \text{CE} \parallel \text{Hg}^{2+} \mid \text{Hg} + \; ; E = \tfrac{1}{2}(E_{10} + E_{20}) + 29.58 \log (\text{Hg}^{2+}) \qquad (8)$$

For the following investigation it was of interest to know how a Hg electrode would behave in solutions where the concentrations of Hg_2^{2+} and Hg^{2+} do not correspond to equilibrium with Hg. One might imagine that the emf would in such cases, depending on the rate of the different relevant reactions, be determined principally by the concentration of Hg_2^{2+} (1), or by that of Hg^{2+} (8), or that Hg would act chiefly as a redox electrode (3). Actually none of these was found to be the case.

To settle the question, a titration was made with both Hg and Pt electrodes, where S contained 4.93 mC Hg_2^{2+} and 0.05 mC Hg^{2+}, and T contained 5.00 mC Hg^{2+}. After equilibrium the concentration of Hg_2^{2+} should therefore be practically unchanged. The results are shown in Table 2. With the first small additions, E_{Hg} scarcely changed at all and even after adding 55 ml, so that $(\text{Hg}_2^{2+}) \approx$

Table 2. *Mercury electrode in* Hg_2^{2+}—Hg^{2+}.

$S = 4.93\ Hg_2^{2+}\ 0.05\ Hg^{2+},\ T = 5.00\ Hg^{2+}$.

v ml	t	E_{Hg}	E_{Pt}
0		454.55	($\sim$455)
2	3m	454.5	
	6m	»	
	10m	»	
5	5m	454.45	
	10m	454.5	
	16m	»	
15	10m	454.45	
	15m	454.5	
35	10m	454.3	
55	5m	454.15	556.25
	16m	454.1	555.3
	21m	»	554.95
	25m	»	554.6
	72m	454.4	550.45
	104m	454.35	546.35
	144m	»	543.75
	24h	454.45	508.7
	36h	454.5	500.8

The times t are counted from the last addition of T. For each value of v the last E was always read immediately before the next addition of T. E_{Hg} and E_{Pt} are not standardized.
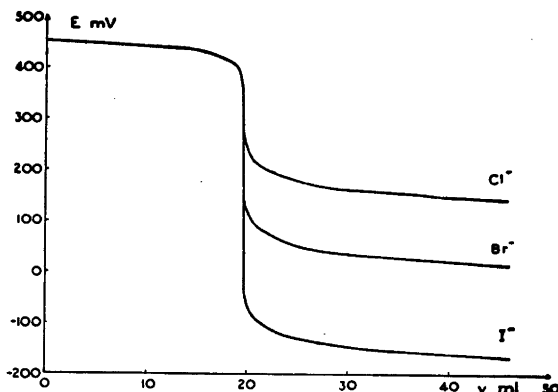
Fig. 1. Titration of 4.9 mC Hg_2^{2+} with 50 mC X^- (= Cl^-, Br^-, and I^-).

3.2 and $(Hg^{2+}) \approx 1.8$, E_{Hg} was only about 0.5 mV lower than the original value, although E_{Pt} had increased by 100 mV. Within an hour, E_{Hg} had moreover returned to a value about 0.1 mV below the original one, and afterwards remained practically constant. During the next few days, the solution was stirred continously, and gradually approached equilibrium as is seen from E_{Pt}, which drifts slowly towards E_{Hg}.

Thus E_{Hg} kept all the time to within a few 0.1 mV of *the value corresponding to the final equilibrium between the solution and Hg metal*, $(Hg_2^{2+}) = 4.94$—$4,95$ mC. In evaluating the potentials of Hg electrodes, we have, therefore, thought it justified to assume that, so long as there are considerable amounts of Hg^{2+} or Hg_2^{2+} ions present, the layer of solution close to the mercury is in equilibrium with the metal in accordance with (4).

TITRATIONS FOR DETERMINING E_{10} AND E_{1X}

In order to obtain E_{10} and E_{1X} we made titrations with a Hg electrode and with the solutions $S = (b - \frac{\delta}{2})$ mC Hg_2^{2+}, δ mC Hg^{2+} and $T = c$ mC X^-. The general course of the $E(v)$ curves with X = Cl, Br, and I is brought out by Fig. 1. Before the equivalence point the curves are practically identical for the three halogens; the latter part of the curve, where X^- is in excess, is highest for Cl^- and lowest for I^-, corresponding to the low solubility of Hg_2I_2.

In the first rather flat part of the curve, there is an excess of Hg_2^{2+}. In this part, the only complexes of bivalent mercury that need be considered are HgX^+ and HgX_2; the concentrations of HgX_3^- and HgX_4^{2-} can be neglected. It is, moreover, assumed that soluble complexes of mercury (I) such as Hg_2X^+ can be neglected. It can be proved that the concentration of free halogen, X^-, is negligible.

2

If it is observed that there may be a transition $Hg^{2+} + Hg = Hg_2^{2+}$; the following equations are found to be valid:

$$(Hg_2^{2+}) + (Hg_2X_2)_{solid} + (Hg^{2+}) + (HgX^+) + (HgX_2) = (Hg^I)_{total} + (Hg^{II})_{total} =$$
$$= 100 \ (b + \tfrac{\delta}{2}) \ (100 + v)^{-1}$$

$$2(Hg_2X_2)_{solid} + (HgX^+) + 2 \ (HgX_2) = (X)_{total} = vc \ (100 + v)^{-1}$$

from which it follows that

$$(Hg_2^{2+}) + (Hg^{2+}) + \tfrac{1}{2} \ (HgX^+) = [100(b + \tfrac{\delta}{2}) - \tfrac{vc}{2}] \ (100 + v)^{-1} = -\tfrac{1}{2} \ X_e \qquad (9)$$

Here X_e is the concentration of halogen in excess over that needed for forming Hg_2X_2 and HgX_2. In the first part of the titration curve, X_e is negative.

The results in Table 2 make it probable that close to the electrode there is equilibrium between bivalent, monovalent and metallic mercury. Under this assumption it is found from (4) and (6) and the definitions of $\varkappa_i$ in Part I that

$$(Hg^{2+}) = k_o^{-1} \ (Hg_2^{2+}); \quad (HgX^+) = \varkappa_1 \sqrt{k_s} \ k_o^{-1} \ \sqrt{(Hg_2^{2+})} \qquad (10)$$

If we insert the values of $\varkappa_1$, k_s and k_o that were found later on during this investigation, we find, expressing all concentrations in mC

$$(Hg^{2+}) = 0.0077 \ (Hg_2^{2+}); \ \tfrac{1}{2} \ (HgCl^+) = 0.0024 \ \sqrt{(Hg_2^{2+})}$$

$$\tfrac{1}{2} \ (HgBr^+) = 0,0028 \ \sqrt{(Hg_2^{2+})}; \ and \ \tfrac{1}{2} \ (HgI^+) = 0.016 \ \sqrt{(Hg_2^{2+})} \qquad (11)$$

(The values for Br and I are preliminary). The millimolar potential E_{10} can be calculated from E by means of (1) which gives

$$E_{10} = E - 29.58 \log (Hg_2^{2+}) = E - 29{,}58 \log (-\tfrac{1}{2}X_e) + \delta E \qquad (12)$$

where according to (9) and (10)

$$\delta E = 29.58 \ \log \ [-\tfrac{1}{2} X_e \ (Hg_2^{2+})^{-1}] = 29.58 \ \log \ [1 + (Hg^{2+}) \ (Hg_2^{2+})^{-1} +$$
$$+ \tfrac{1}{2} \ (HgX^+) \ (Hg_2^{2+})^{-1}] \approx 12.85 \ [(Hg^{2+}) \ (Hg_2^{2+})^{-1} + \tfrac{1}{2} (HgX^+) \ (Hg_2^{2+})^{-1}] =$$
$$= 12.85 \ k_o^{-1} + 6.42 \ \varkappa_1 \ k_o^{-1} \sqrt{k_s} \ (Hg_2^{2+})^{-\frac{1}{2}} \qquad (13)$$

As (Hg_2^{2+}) is only slightly smaller than $(-\tfrac{1}{2} X_e)$, the correction δE is rather small. By inserting the numerical values into (12) we find e. g.:

$(Hg_2^{2+}) = 4$ mC $\quad \delta E = 0.115$ mV for Cl and Br, $\quad$ 0.20 mV for I

$(Hg_2^{2+}) = 1$ mC $\qquad\quad$ 0.13 mV for Cl and Br $\qquad$ 0.30 mV for I

$(Hg_2^{2+}) = 0.25$ mC $\qquad$ 0.16 mV for Cl and Br $\qquad$ 0.50 mV for I $\quad$ (14)

At $v = 0$, before any X^- has been added, δE is in all cases 0.10 mV.

Table 3 gives a few typical titrations of Hg_2^{2+} with Cl^-. The constancy of E_{10} shows that our fundamental assumptions are probably true, and especially that complexes Hg_2Cl^+ are not formed in considerable amounts.

Table 3. Titrations for E_{10} and E_{1X}.

$S = 4.832$ mC Hg_2^{2+}, $\ 0.040$ mC Hg^{2+}.

$T = 50.00$ mC Cl^-.

v ml	$\frac{1}{2}X_e$ mC	29.58 log (Hg_2^{2+}) mV	E mV	CE »A»		CE »G»		E average	E_{10}
0	4.872	20.24	453.85	453.9	453.7	454.8	454.9	454.8_3	434.5_9
2	4.286	18.59		452.2	452.1	453.1	453.1	453.1_3	434.5_4
4	3.723	16.78		450.4	450.4	451.4	451.3	451.3_8	434.6_0
6	3.181	14.75		448.35	448.3	449.3	449.3	449.3_1	434.5_6
8	2.659	12.44		446.0	446.0	446.9	446.9	446.9_5	434.5_1
10	2.156	9.75	443.4	443.3	443.3	444.7	444.2	444.3_8	434.6_3
12	1.671	6.50			440.2	441.1	440.9	441.0_7	434.5_7
15	0.975_7	—0.45	433.3					(434.3)	(434.7_5)
17	0.531_6	—8.26	425.5					(426.5)	(434 7_6)
19	0.102_5	—29.45	403.9					(404.9)	(434.3_5)
	X_s	59.16 log X_s mV							E_{1X}
20	0.213	—39.70	239.9					(240.9)	(201.2_0)
21	0.625	—12.08	212.85					(213.8_5)	(201.7_7)
30	4.043	35.89	164.7					(165.7)	(201.5_9)
35	5.745	44.92	155.9	155.7				156.8_0	201.7_2
40	7.326	51.16	149.1	149.2	150.0	150.8	150.8	150.5_8	201.7_4
45	8.797	55.87		144.3	144.3	145.3		145.3_0	201.1_7
50	10.171	59.59		140.5	140.9	141.9	141.9	141.8_0	201.3_9

For each value of v (the volume added), X_s and 29.58 log (Hg_2^{2+}) have been calculated with the aid of (9), (12) and (14). The emf:s were measured with two different CE:s, »A» and »G»; Before the average was taken, 1.0 mV was added to the emf:s with »A». Average of the values for 0—12 ml and 30—50 ml:

$$E_{10} = 434.5_7, \quad E_{1X} = 201.5_2$$

The equilibrium conditions for Hg_2X^+ would be

$$Hg_2X_2(s) + Hg_2^{2+} = 2Hg_2X^+ \qquad K = (Hg_2X^+)^2(Hg_2^{2+})^{-1} \qquad (15)$$
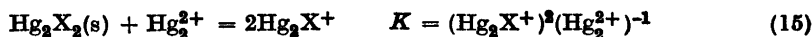
The Hg_2X^+ present would cause an additional term $\frac{1}{2}(Hg_2X^+)$ to the left in (9) and thus an addition to δE

$$\delta' E = 29.58 \log [1 + \frac{1}{2}(Hg_2X^+)(Hg_2^{2+})^{-1}] \approx 6.42 \ (Hg_2X^+) \ (Hg_2^{2+})^{-1} =$$
$$= 6.42 \sqrt{K} \ (Hg_2^{2+})^{-\frac{1}{2}} \qquad (16)$$

If the amount of Hg_2X^+ were considerable, there would be a decrease in the calculated E_{10} between $v = 0$ (where no X has been added) and, for example, $v = 2$ ml. Actually no such decrease could be proved to exist for Cl, Br or I. In any case it never seemed to amount to as much as 0.2 mV, which according to (16) means that K is less than $5.10^{-6}C$. Even if this value were attained, the k_{12} calculated in Part II[2] for Hg^{2+} —Cl⁻ and Br⁻ would not be significantly changed. (The value of k_{12} for I⁻ is in any case rather uncertain). In the »E_{max} titration» to be described in Parts IV and V, no error at all would be caused by disregarding Hg_2X^+.

During our investigations the difference E_{20}—E_{10} was determined on several occasions, using different stock solutions and different CE:s. The results are summarized in Table 4; each pair of values given was measured with the same CE and within a short time interval.

Table 4. Measurements of E_{20} and E_{10}.

Month	CE	E_{20}	E_{10}	E_{20}—E_{10}
7. 1945	»G»	559.7	434.7	125.0
»	»A»	559.6	434.8	124.8
5. 1946	»G»	559.1	434.0	125.1
»	»G»	559.2	434.5	124.7
7. 1946	»A»	559.1	433.6	(125.5)*
»	»G»	559.3	434.6	124.7
8. 1946	»A»	558.3	433.6	124.7
»	»A»	558.6	433.6	125.0
»	»G»	559.5	434.6	124.9
9. 1946	»A»	559.2	433.9	(125.3)*
10. 1946	»A»	558.9	433.9	125.0

Average 124.9 $\pm$ 0.2

We have excluded the measurements of E_{20} made with one particular stock solution of Hg^{2+} which was prepared in November, 1945, and proved later on to have been contaminated.

With two exceptions, marked with an asterisk, the difference $E_{20}—E_{10} = 59.16 \log k_o$ is seen to lie within the limits

$$59.16 \log k_o = 124.9 \pm 0.2 \text{ mV} \tag{17}$$

With the first less accurate apparatus (see Part I), Inger Brattsten, *legitimerad apotekare*, found $E_{20}—E_{10} = 558.0—432.7 = 125.3$ mV, whereas Mrs Inga Westöö found $558.0—433.4 = 124.6$ mV. These values are seen not to be very far from our final average.

From (17) follows

$$\log k_o = 2.111_2 \pm 0.003_4 \quad ; \quad k_o = 129.2 \pm 1.0 \tag{18}$$

This constant has previously been determined analytically by Ogg (1898)[3] who found 100—120 (the temperature was not mentioned) and by Abel (1901)[4] who found 120 at 25° C. Latimer [5] calculated k_o for infinite dilution from the standard potentials of mercury; he found 81, but as the extrapolation of the redox potential to infinite dilution is uncertain to within about 5 mV, this k_o is not very accurate. As the activity factors of the two bivalent ions can be expected approximately to cancel out one another, k_o should not vary very much with the ionic strength. However, the effect of varying acidity may be considerable and this is probably the chief reason for the incertainty of an extrapolation to infinite dilution.

From (17) we find, standardizing E_{10} to 434.5 mV

$$E_{10}^{st} = 434.5 \text{ mV} \qquad E_{20}^{st} = 559.4 \pm 0.2 \text{ mV} \tag{19}$$

From (8) and (19) we find for any Hg electrode

$$E^{st} = 496.95 \ (\pm 0.10) + 29.58 \log (Hg^{2+}) \tag{20}$$

This expression will prove useful in subsequent work.

E_{1X} AND k_s FOR Hg_2Cl_2

After the equivalence point, there is a new flat part of the titration curve $E(v)$ in Fig. 1. From this part of the titration it is possible to calculate E_{1X} and thus k_s for Hg_2X_2 by means of (2) and (6). The excess of halogen

$$X_e = [vc — 200(b + \tfrac{\delta}{2})] \ (100 + v)^{-1} \tag{9a}$$

is positive and one might ask if it is permissible to assume $X_{\bullet} = X$, (or (X^-)), the concentration of free X^- ions). Certainly all previous experimental evidence speaks against the existence of considerable amounts of soluble complexes $Hg_2X_3^-$ and the like at moderate X^- concentrations. However, in equilibrium with Hg metal, solid Hg_2X_2, and X^- there is always a certain amount of HgX_2, HgX_3^-, and HgX_4^{2-}, and it can be shown that

$$X_{\bullet} = (X^-) + (HgX_3^-) + 2(HgX_4^{2-}) = X \left(1 + \varkappa_3 k_s k_o^{-1} + 2 \varkappa_4 k_s k_o^{-1} X\right) \quad (21)$$

If the numerical values of the equilibrium constants for Cl are inserted, it is found that the two constant factors to the right in (21) are about 10^{-5} and $2 \cdot 10^{-7}$ mC^{-1}, and can thus be neglected. Consequently it seems permissible to use $X_{\bullet}$ instead of (X^-) in (2).

In the latter part of Table 3 are given particulars of a few titrations, whereas Table 5 gives average values of E_{10} and E_{1X} for a number of titrations. As in

Table 5. Measurements of E_{10} and E_{1X}.

Month	E_{10}	E_{1X}	$E_{10}-E_{1X}$
7. 1945	434.7	201.9	232.8
12. 1945	434.3	201.1	233.2
»	434.2	200.9	233.3
6. 1946	435.5	202.2	233.3
7. 1946	433.6	200.5	233.1
»	434.6	201.5	233.3

Average 233.1 ± 0.3

each titration the E_{1X} values for different v often differ by 0.2—0.3 mV, whereas the difference in E_{10} or E_{20} in the same titration are usually only 0.1 mV, it seems safe to give here broader limits of error,

$$E_{10} - E_{1X} = - 29.58 \log k_s = 233.1 \pm 0.3 \text{ mV} \quad (22)$$

from which follows

$$\log k_s = 0.120 \pm 0.010 - 8;$$

$$k_s = (1.32 \pm 0.03) \cdot 10^{-8} \text{ mC}^3 = (1.32 \pm 0.03) \cdot 10^{-17} \text{ C}^3 = (Hg_2^{2+}) \, (Cl^-)^2 \quad (23)$$

$$E_{1X}^{st} = 201.4 \pm 0.3 \text{ mV} \quad (24)$$

According to Brodsky and Scherschewer (1926) the activity product of Hg_2Cl_2 at 25°C is $K_s = 1.15 \cdot 10^{-18}$. If this value is assumed to be correct, the product of the activity factors in our solutions should be about 0.1, which seems reasonable.

Experimental note: After the equivalence point, the emf was at first higher than the final value, which was not attained until after several hours. Our observations could be explained by the assumption that the precipitate is at first very fine-grained and therefore more soluble than are larger grains. Thus when the solution was stirred before equilibrium had been reached, the potential was too high (both small and large grains smashed against the mercury surface). If the stirrer was stopped, the emf sank to a value close to the final equilibrium emf, as the larger grains are the first to sink down to the mercury surface.

In one instance the titration of Hg_2^{2+} was started in the evening. When a certain excess of Cl^- had been added, after about an hour the emf was 181.0 mV with vigorous stirring, 180.8 mV with moderate stirring, and 180.6 mV if the stirring was stopped for a while; these emf:s could be reproduced at will. Next morning, the emf was still 180.6 mV without stirring but increased to 180.7 mV if a vigorous stirring was applied.

SUMMARY

Under the experimental conditions chosen: 25° C, $(H^+) = 10$ mC, $(X^-) + (ClO_4^-) = 500$ mC, the following »millimolar potentials» (see 1—3) were found:

$$E_{10}^{st} = 434.5 \text{ (standard value)}, \quad E_{20}^{st} = 559.4 \pm 0.2, \quad E_{1X}^{st} = 201.4 \pm 0.3 \text{ (for Cl)}$$

The following equilibrium constants were calculated:

$$Hg^{2+} + Hg = Hg_2^{2+} \qquad k_o = 129.2 \pm 1.0$$
$$Hg_2Cl_2(s) = Hg_2^{2+} + 2\ Cl^- \qquad k_s = (1.32 \pm 0.03).10^{-17}\ C^3$$

It was shown that a mercury electrode in a solution containing Hg^{2+} and Hg_2^{2+} quickly acquired the potential corresponding to the final equilibrium between the solution and Hg metal. During a titration of Hg_2^{2+} with halogen X^-, corrections should be made for the presence of Hg^{2+} and its complexes with X^-. Expressions are given for these corrections. No appreciable amounts of soluble complexes Hg_2X^+ could be detected.

The effect of stirring on the electrode potential of Hg in a newly precipitated suspension of Hg_2X_2 in an X^- solution is discussed.

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