

Electrometric Investigation of Equilibria between Mercury and Halogen Ions

V. Complexes between Hg^{2+} and Cl^-

BENGT LINDGREN, ARNE JONSSON and
LARS GUNNAR SILLÉN

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

This paper is concerned with the equilibrium constants of the reactions between Hg^{2+} and Cl^- , leading to the formation of HgCl^+ , HgCl_2 , HgCl_3^- , and HgCl_4^{2-} ; from these constants a few equilibria with Hg metal and Hg_2Cl_2 have also been calculated.

In part I¹ of this series, the complex products κ_i were defined by (I,1) ($X = (\text{X}^-)$, the concentration of free halogen ions):

$$\begin{aligned} \kappa_1 &= (\text{HgX}^+)(\text{Hg}^{2+})^{-1}X^{-1}, & \kappa_2 &= (\text{HgX}_2)(\text{Hg}^{2+})^{-1}X^{-2} \\ \kappa_3 &= (\text{HgX}_3^-)(\text{Hg}^{2+})^{-1}X^{-3}, & \kappa_4 &= (\text{HgX}_4^{2-})(\text{Hg}^{2+})^{-1}X^{-4} \end{aligned} \quad (1)$$

and the equilibrium constants q_1 and q_2 by (I,2)

$$\begin{aligned} q_1 &= (\text{HgX}_3^-)(\text{HgX}_2)^{-1}X^{-1} = \kappa_3 \kappa_2^{-1} \\ q_2 &= (\text{HgX}_4^{2-})(\text{HgX}_2)^{-1}X^{-2} = \kappa_4 \kappa_2^{-1} \end{aligned} \quad (2)$$

In part IV² of this series was demonstrated how the complex constants κ_i can be calculated from the data recorded in I—III, together with redox titrations with halogen X^- of a mixture of Hg^{2+} and Hg_2^{2+} , in the presence of an excess of solid Hg_2X_2 . The course of the E curve is shown in Fig. 1, part IV; from its first part κ_1 and κ_2 can be calculated, from its latter part q_1 and q_2 , and thus κ_3 and κ_4 .

The apparatus used was described in Part I, where the reasons were also given that made us study these equilibria at constant (H^+) and constant ionic strength.

The measurements recorded in part II³ led to the equilibrium constant:

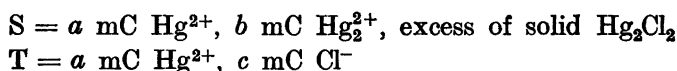
$$k_{12} = (\text{HgX}^+)^2(\text{HgX}_2)^{-1}(\text{Hg}^{2+})^{-1} = \kappa_1^2 \kappa_2^{-1} = 1.80 \pm 0.10 \text{ for X = Cl} \quad (3)$$

In part III⁴ are given measurements of the »millimolar potentials» E_{10} and E_{20} and E_{1X} defined by (I, 3—5) or (III, 1—3). The average values found were (in mV):

$$\begin{aligned} E_{10} &= 434.5, E_{20} = 559.4 \pm 0.2, E_{1X} = 201.4 \pm 0.3 \text{ (for Cl)} \\ -29.58 \log k_s &= 233.1 \pm 0.3 \end{aligned} \quad (4)$$

TITRATIONS FOR E_{\max}

In order to obtain κ_1 and κ_2 we made titrations with Pt electrodes, where v ml of T was added to 100 ml of S, and



When S was mixed, either the amount of Hg_2^{2+} was chosen rather large, and Cl^- was added so that Hg_2Cl_2 precipitated in the original 100 ml of S, or Hg_2Cl_2 was prepared by precipitation in a separate container, washed, moistened with (490 mC NaClO_4 , 10 mC HClO_4) and added to S. The amount of Hg_2Cl_2 was 1—5 g in 100 ml.

It was demonstrated in part IV that all the information needed can be obtained from E_{\max} , the maximum value of E . Sometimes a rather quick titration was made at first without waiting for equilibrium after each new addition of T. This was to ascertain the approximate position of the maximum, which could also be calculated as soon as approximate values of the equilibrium constants had been obtained. Then a new titration was made with the same concentrations but with more careful measurements especially in the neighbourhood of E_{\max} .

Generally, after every new addition of Cl^- , the emf was at first 1—2 mV below its final value, which was only obtained after $\frac{1}{2}$ —2 hours of stirring.

Table 1 gives the values of E_{\max} found for different values of a . The column »corr» gives the correction to be added to all emf:s measured with the CE employed in order to make E_{10} and E_{20} equal to their »standardized» values (4). Some of these measurements were made by Inger Brattsten, *leg. apot.*

It is required by (IV,6) that $(E_{\max} - 59.16 \log a)$ should be a constant, independent of a . As seen from Table 1, there is a certain variation in the values found for this quantity but this is not systematic with a .

Table 1. Titrations for E_{\max} .

a	$59.16 \log a$	E_{\max}	Corr	$E_{\max}^{\text{st}} - 59.16 \log a$
10.00	59.2	605.5	+ 1.8	548.1
10.00	59.2	605.6	+ 1.8	548.2
5.170	42.2	590.0	+ 0.3	548.1
5.100	41.9	589.0	+ 0.3	547.4
2.788	26.3	572.6	+ 1.6	547.9
2.788	26.3	572.4	+ 1.4	547.5
2.180	20.0	568.5	+ 0.3	548.8
				Average 548.0 ± 0.5

We thus feel justified in assuming that we have really obtained the equilibrium assumed in IV, and accept the average value:

$$E_{\max} - 59.16 \log a = 548.0 \pm 0.5 \text{ mV} \quad (5)$$

If we insert the numerical values into (IV,6) we find

$$548.0 \pm 0.5 = E_{20} + E_{10} - E_{1x} - 59.16 \log (2 + \sqrt{k_{12}}) - 29.58 \log \kappa_2 = 559.4 \pm 0.2 + 233.1 \pm 0.3 - 31.0 \pm 0.3 - 29.58 \log \kappa_2$$

which leads to

$$29.58 \log \kappa_2 = 213.5 \pm 0.7 \quad (6)$$

$$\log \kappa_2 = 7.21_8 \pm 0.02_4 \text{ (mC scale)}$$

$$\kappa_2 = (1.65 \pm 0.10) \cdot 10^7 \text{ mC}^{-2} = (1.65 \pm 0.10) \cdot 10^{13} \text{ C}^{-2} \quad (7)$$

Now from (7) and (3) we find

$$2 \log \kappa_1 = \log \kappa_2 + \log k_{12} = 7.21_8 \pm 0.02_4 + 0.25_5 \pm 0.02_5 = 7.47_3 \pm 0.03_5$$

$$\log \kappa_1 = 3.73_6 \pm 0.01_8 \text{ (mC scale)}$$

$$\kappa_1 = (5.4_5 \pm 0.2_3) \cdot 10^3 \text{ mC}^{-1} = (5.4_5 \pm 0.2_3) \cdot 10^6 \text{ C}^{-1} \quad (8)$$

We have used (IV,14) and (IV,15) to calculate the course of E during two titrations, where

$$S = 10.0 \text{ Hg}^{2+}, 1.0 \text{ Hg}_2^{2+}, \text{ excess of Hg}_2\text{Cl}_2$$

$$T = 10.0 \text{ Hg}^{2+}, 100 \text{ Cl}^-$$

Inserting the equilibrium constants obtained, we find from (IV,14) and (IV,15)

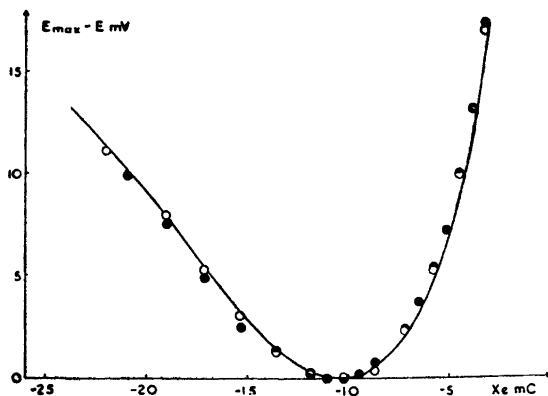


Fig. 1. Titration for E_{\max} with $S = 10.0 \text{ Hg}^{2+}$, 1.0 Hg_2^{2+} , excess of Hg_2Cl_2 , $T = 10.0 \text{ Hg}^{2+}$, 100 Cl^- . Filled and open circles: results of two different experiments. Curve = calculated values.

$$E_{\max} - E = 59.16 \log[(1.3416 + z + z^{-1}) \cdot 3.3416^{-1}] \quad (9)$$

$$-X_e = 0.436 z^2 + 10(1.3416 + 2z^{-1})(1.3416 + z + z^{-1})^{-1} \quad (10)$$

where z is a parameter which has the value 1 at E_{\max}

On the other hand, from the composition of S and T we find that after addition of v ml of T to 100 ml of S, the deficiency in halogen is

$$-X_e = (2200 - 80 v)(100 + v)^{-1} \quad (11)$$

In Fig. 1, $(E_{\max} - E)$ is plotted against $-X_e$. The curve has been drawn through points calculated for round values of z by means of (9) and (10). The circles are the experimental data from the two titrations; X_e has been calculated by means of (11). The experimental points are seen to follow the theoretical curve very well, except that they all seem to be shifted slightly, 0.2–0.3 mC, in the direction of negative X_e . This constant shift seems to indicate that the halogen content was slightly larger than calculated; the most probable explanation seems to be that the Hg_2Cl_2 (which was prepared in these experiments outside the solution) had adsorbed a slight excess of halogen ions.

The good agreement is taken as additional proof that real equilibria have been studied and that the theoretical treatment in Part IV is applicable.

PREVIOUS MEASUREMENTS OF κ_1 AND κ_2

The most recent measurements of κ_1 and κ_2 known to us are more than thirty years old and are subject to the objections mentioned in part I in this series.

Luther⁵ tried two different ways of calculating κ_2 . Firstly, from the measurements of other workers on the half-cells Pt, Hg₂Cl₂(s)/HgCl₂, Cl⁻; Hg, Hg₂Cl₂(s)/Cl⁻, and Hg/Hg₂²⁺, and of the equilibrium Hg²⁺ + Hg = Hg₂²⁺ he found $\kappa_2^{-1} = 1.5 \cdot 10^{-14}$, thus $\kappa_2 = 6.7 \cdot 10^{13} \text{ C}^{-2}$ at about 16° C. A second value was calculated from the solubility of AgCl in Hg²⁺ solutions; this calculation was erroneous because Luther did not take into account the formation of HgCl⁺ ions, the existence of which was proved in the following years by Morse⁶. From the solubility of AgCl in Hg⁺ solutions, Morse calculated $\kappa_1^{-1} = 3.5 \cdot 10^{-8}$, thus $\kappa_1 = 2.9 \cdot 10^7 \text{ C}^{-1}$ at 25° C. From the distribution of HgCl₂ between toluene and aqueous Hg(NO₃)₂ solutions he found $k_{12}^{-1} = 0.13$, which with Morse's value of κ_1 gives $\kappa_2 = 10^{14} \text{ C}^{-2}$ at 25° C. The same value of κ_2 , 10^{14} , was also found by Sherrill⁷ from rather uncertain calculations.

From the solubility of AgCl in solutions containing Hg²⁺ and an excess of Ag⁺ or Cl⁻, Buttle and Hewitt⁸ found $\kappa_1^{-1} = 5.3 \cdot 10^{-8}$, thus $\kappa_1 = 1.9 \cdot 10^7 \text{ C}^{-1}$ at 25° C. Drucker (1912) used Luther's first method with more accurate data to recalculate $\kappa_2^{-1} = 9.4 \cdot 10^{-15}$, thus $\kappa_2 = 1.06 \cdot 10^{14} \text{ C}^{-2}$ at 25° C.

TITRATIONS FOR q_1 AND q_2

The titrations for determining q_1 and q_2 were carried out as indicated in part IV, *i. e.* with excess of solid Hg₂Cl₂, excess of Cl⁻ (positive X_c) and with a constant total concentration a of Hg^{II}.

In Table 2 are given data for two titrations, A1 and A2, with CE »A» and S = 2.00 mC HgCl₂ 6.0 mC Cl⁻ (20 mC Hg₂Cl₂ (s))

T = 2.00 mC HgCl₂ 482 mC Cl⁻

Table 3 gives two other titrations, G1 and G2, with CE »G» and

S = 5.00 mC HgCl₂ (20 mC Hg₂Cl₂ (s))

T = 5.00 mC HgCl₂ 470 mC Cl⁻

In all these titrations Hg₂Cl₂ was precipitated in S when it was being mixed.

After each new addition of T, the emf seemed to become constant within 15—30 minutes at lower Cl⁻ concentrations, within 10 minutes at the higher ones. The emf:s were well defined; different Pt electrodes, however, often showed slightly different emf:s.

In each titration two different platinum electrodes were used. An asterisk shows that the electrode has been »burnt out» in an alcohol flame. After burning, the emf was at first several 10 mV higher than before but rapidly sank and after $\frac{1}{2}$ —2 hours attained a value, 1—2 mV higher than that of »old» electrodes. The high value may then be retained for many hours. This is clearly brought out by a comparison of the emf:s of titration A1, where the electrodes were burnt out, with those of A2, where »older» electrodes

Table 2. Titration for q_1 and q_2 . $S = 2.00$ mC $HgCl_2$, 60 mC Cl^- ; $T = 2.00$ mC $HgCl_2$, 482 mC Cl^- , CE »A».

v ml	X_c mC	X mC	E mV				E_{calc} $q_1 = 7, q_2 = 70$
			A1		A2		
0	6.00	5.91	*335.4	*335.6	331.5	331.5	335.6
2	15.33	15.08	310.2	310.5	306.7	307.1	309.6
4	24.31	23.90	296.5	296.7	293.4	293.7	295.9
6	32.94	32.36	287.3	*	283.9	284.3	286.2
8	41.26	40.53	279.3	(283.7)	276.6	277.0	278.6
10	49.27	48.38	272.7	(275.8)	270.4	270.9	272.2
12	57.00	55.96	266.4	268.8	265.0	265.7	266.8
14	64.46	63.29	261.8	263.6	260.1	260.5	261.8
16	71.66	70.37	*(271.1)	*(268.9)	255.6	256.0	257.4
18	78.61	77.21	254.3	254.1			253.4
20	85.33	83.83	250.1	250.2	248.0	248.2	249.7
25	101.20	99.46	242.1	242.0	240.0	240.4	241.8
30	115.85	113.92	235.3	235.2	233.4	233.7	235.1
35	129.41	127.32	229.6	229.5	227.8	228.0	229.3
40	142.06	139.78	224.7	224.8			224.3
45	153.72	151.39			219.2	219.5	220.0
46	155.97	153.61	219.8	219.8			219.1
50	164.67	162.23	216.7	216.7	215.7	215.8	216.1

Table 3. Titration for q_1 and q_2 . $S = 5.00$ mC $HgCl_2$, $T = 5.10$ mC $HgCl_2$, 470 mC Cl^- , CE »G».

v ml	X_c mC	X mC	E mV				E_{calc} $q_1 = 8.5, q_2 = 7$	
			G1		G2			
8	34.81	33.33	308.5	309.3	307.5	307.3	308.9	309.9
10	42.73	40.88	301.4	301.7	300.7	300.6	301.7	302.9
12	50.36	48.15	*(298.9)	295.2	294.7	294.7	295.7	296.9
14	57.72	55.18	291.3	290.1	290.2	290.4	290.5	291.8
16	64.83	61.98	286.9	285.5	285.5	285.5	285.5	287.2
18	71.69	68.54	282.0	281.0	281.3	281.3	281.6	283.1
20	78.33	74.91	278.2	277.2	277.5	277.5	277.8	279.3
25	94.00	89.99	270.1		269.3	269.3	269.5	271.1
30	108.46	103.95	263.0	262.4	262.1	262.1	262.7	264.2
35	121.85	116.93	257.1	256.5	256.4	256.5	256.7	258.3
40	134.29	129.02	252.2	251.3	251.4	251.4	251.6	253.2
45	145.86	140.29	247.5	247.5	246.9	247.0	247.1	248.6
50	156.67	150.86	243.7	243.7	243.3	243.3	243.2	244.7

were used, and with G1, where one electrode was burnt. During the course of A1, »old» electrodes were sometimes inserted in the solution and then gave potentials close to those of A2. The cause of the difference was thus in the Pt electrodes, not in, for example, errors in the composition of the solution.

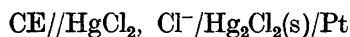
The figures in Tables 2 and 3 should give an impression of what sort of accuracy could be attained in our measurements. If the first points are omitted, where the emf:s are sensitive to very small changes in the composition and where moreover the potentials were less steady, then the emf:s are seen to be defined to within one mV in G1 and G2, and to within 2 mV if A1 and A2 are compared. Carter and Robinson¹⁰ seem to have had much worse experience with half-cells Pt, Hg₂Cl₂/HgCl₂, Cl⁻. Even at high (Cl⁻) and after several days their emf:s were unsteady to within several mV. Maybe we owe our more constant results to continual vigorous stirring.

According to (IV,16) (IV,17), (4) and (6):

$$E = E_{2x} + 59.16 \log (\text{HgX}_2) - 59.16 \log X \quad (12)$$

$$E_{2x} = E_{20} + E_{10} - E_{1x} - 59.16 \log \kappa_2 = 559.4 \pm 0.2 + 233.1 \pm 0.3 - 427.0 \pm 1.4 = 365.5 \pm 1.5 \text{ mV} \quad (13)$$

The value of E_{2x} can also be found by direct measurements of cells



at low (Cl⁻) where the formation of HgCl₃⁻ can be neglected or easily corrected for. Such measurements were tried by Inger Brattsten, *leg. apot.*, who found values of E_{2x} (after standardization) ranging from 364.5 to 368 mV, which is in good agreement with (13) in view of the difficulty of the measurements.

The calculations were carried out as indicated in part IV, with the aid of equation (IV,22):

$$59.16 \log r = 59.16 \log (1 + q_1X + q_2X^2) = E_{2x} + 59.16 \log a - E - 59.16 \log X \quad (14)$$

The individual correction to the emf:s measured with CE »A» was at that time + 1.0 mV, for »G» 0 mV. From the first approximate plotting of $(r'-1)X_e^{-1}$ against X_e , the approximate values $q_1 = 0.007 \text{ mC}^{-1} = 7 \text{ C}^{-1}$, $q_2 = 0.00007 \text{ mC}^{-2} = 70 \text{ C}^{-2}$ were chosen. Using these constants better values of $X = (\text{Cl}^-)$ were calculated, which are given in Tables 2 and 3. A graph according to (IV,23) was then made of

$$F_1 = (r - 1)X^{-1} = q_1 + q_2X \quad (15)$$

against X for the different titrations, which is given in Fig. 2.

In Fig. 2, the points for $X < 50 \text{ mC}$ can be disregarded, as a small error in E_{2x} or in X with cause a large displacement of these points and moreover less care was for this reason taken in waiting for the equilibrium E .

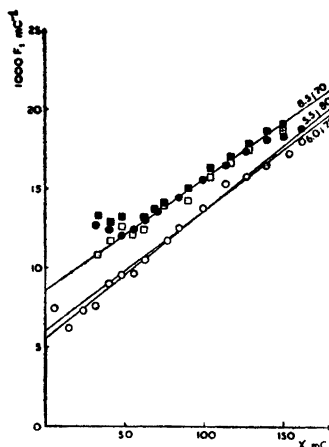


Fig. 2. Function $F_1(X)$ from different titrations for q_1 and q_2 . Squares: titrations with $a = 5$ mC. Open squares: G1, filled: G2. Circles: titrations with $a = 2$ mC. Open circles: A1, filled: A2 (see Tables 2 and 3). Upper line: $F_1(X)$ calculated with $q_1 = 8.5$ C $^{-1}$, $q_2 = 70$ C $^{-2}$. Lower lines: calculated with q_1 and $q_2 = 5.5$ and 80 , or 6.0 and 75 .

It is seen that the points for the titrations A2, G1 and G2 fit rather well to the straight line $F_1 = 8.5 \cdot 10^{-3}X + 70 \cdot 10^{-6}X^2$ corresponding to $q_1 = 8.5 \cdot 10^{-3} \text{mC}^{-1} = 8.5$ C $^{-1}$ and $q_2 = 70 \cdot 10^{-6} \text{mC}^{-2} = 70$ C $^{-2}$.

On the other hand, the points of A1 (where the electrodes were burnt) are considerably lower; the two lower lines drawn in Fig. 2 correspond to $q_1 = 5.5$ C $^{-1}$, $q_2 = 80$ C $^{-2}$ and $q_1 = 6.0$ C $^{-1}$, $q_2 = 75$ C $^{-2}$.

An increase or decrease in E_{2x} by 1.5 mV will increase or decrease F_1 by about 1.5 C $^{-1}$ for all except for the lowest X . The inaccuracy in E_{2x} according to (13) means an inaccuracy in q_1 of about 1.5 C $^{-1}$, whereas q_2 is not appreciably affected.

Of the three lines in Fig. 2 we are personally inclined to prefer the higher one, which was obtained with old electrodes. However, we do not claim the accuracy to be better than

$$q_1 = (7 \pm 3) \text{C}^{-1} = 10^{0.85 \pm 0.15}$$

$$q_2 = (70 \pm 10) \text{C}^{-2} = 10^{1.85 \pm 0.05}$$

Table 2 gives the emf:s calculated for different v assuming the constants be 7 and 70, and Table 3 the emf:s calculated for $q_2 = 70$ and $q_1 = 7$ or 8.5. The agreement is seen to be as good as can be expected.

Inger Brattsten, *leg. apot.*, made similar titrations with the first apparatus (see part I). It was much more difficult to get reproducible results with the earlier type of Pt electrodes than with the present type, where the glass-Pt seal is well above the aqueous solution.

The average of her determinations was $q_1 = 5.5$ C $^{-1}$, $q_2 = 75$ C $^{-2}$ which is well within the limits of accuracy given above.

According to Linhart¹¹ the equilibrium constant (Hg₂Cl₄) (HgCl₂)⁻² is 0.3 C⁻¹ at 25° C. If the order of magnitude is correct, which we do not doubt, the amount of binuclear complexes must be negligible at the low mercury concentrations we have used. Nor is there anything in our results forcing us to assume the formation of binuclear complexes.

PREVIOUS DETERMINATIONS OF q_1 AND q_2

As far as we know, the equilibria of HgCl₂ with HgCl₃⁻ and HgCl₄²⁻ have hitherto been studied only by partition or solubility equilibria and by optical methods. Sherrill⁷ measured the partition of HgCl₂ between benzene and aqueous KCl solutions at 25° C. He assumed that only HgCl₄²⁻ is formed, but found values of q_2 ranging from 6000 to 82. Out of this range he chose the value 90 which seems to be of the right order of magnitude. Sand and Breest¹⁰ pointed out that Sherrill's measurements could be explained by the formation of HgCl₃⁻ with $q_1 = 11.5$ C⁻¹. Drucker⁹ recalculated q_1 from Sherrill's results, with a correction for the «degree of dissociation» of KCl; he found $q_1 = 13.5$ C⁻¹. Linhart¹³ measured the partition of HgCl₂ between benzene and NaCl solution and found $q_1 = 9.8$ C⁻¹, $q_2/q_1 = 4.9$ C⁻¹, i. e. $q_2 = 48$ C⁻² at 25° C. Job¹⁴ from spectrographic measurements concluded $q_1 = 5$ C⁻¹ (16° C).

Garrett¹⁵ has concluded $q_1 \approx 20$ at 25° C from measurements of the solubility of HgCl₂ in chloride solutions. Garrett assumed that the concentration of HgCl₄²⁻ is negligible, which does not agree with our results.

Table 4. Summary of equilibrium constants.

Reaction	Equilibrium constant	log of equil. const. (C scale)
Hg ²⁺ + Cl ⁻ = HgCl ⁺	$\kappa_1 = \sqrt{k_{12}\kappa_2} = (5.4_5 \pm 0.2_3) 10^6 \text{C}^{-1}$	6.73 ₆ ± 0.018
Hg ²⁺ + 2Cl ⁻ = HgCl ₂	$\kappa_2 = (1.65 \pm 0.10) \cdot 10^{13} \text{C}^{-2}$	13.21 ₃ ± 0.02 ₄
Hg ²⁺ + HgCl ₂ = 2HgCl ⁺	$k_{12} = 1.80 \pm 0.10$	0.255 ± 0.025
HgCl ₂ + Cl ⁻ = HgCl ₃ ⁻	$q_1 = (7 \pm 3) \text{C}^{-1}$	0.85 ± 0.15
HgCl ₂ + 2Cl ⁻ = HgCl ₄ ²⁻	$q_2 = (70 \pm 10) \text{C}^{-2}$	1.85 ± 0.05
Hg ²⁺ + 3Cl ⁻ = HgCl ₃ ⁻	$\kappa_3 = q_1 \kappa_2 = (1.2 \pm 0.5) \cdot 10^{14} \text{C}^{-3}$	14.07 ± 0.15
Hg ²⁺ + 4Cl ⁻ = HgCl ₄ ²⁻	$\kappa_4 = q_2 \kappa_2 = (1.2 \pm 0.2) \cdot 10^{15} \text{C}^{-4}$	15.07 ± 0.06
2HgCl ₂ = HgCl ⁺ + HgCl ₃ ⁻	$q_1 k_{12} \kappa_2^{-\frac{1}{2}} = (2.3 \pm 1.0) \cdot 10^{-6}$	(0.37 ± 0.15) — 6
Hg ₂ Cl ₂ (s) = Hg ₂ ²⁺ + 2Cl ⁻	$k_3 = (1.32 \pm 0.03) 10^{-17} \text{C}^3$	(0.120 ± 0.010) — 17
Hg ₂ Cl ₂ + 2Hg ²⁺ = Hg ₂ ²⁺ + 2HgCl ⁺	$k_3 k_{12} \kappa_2 = (3.9 \pm 0.4) 10^{-4} \text{C}$	(0.593 ± 0.036) — 4
Hg + Hg ²⁺ = Hg ₂ ²⁺	$k_0 = 129.2 \pm 1.0$	2.111 ₂ ± 0.003 ₄
Hg ₂ Cl ₂ = Hg + HgCl ₂	$k_3 \kappa_2 k_0^{-1} = (1.7 \pm 0.1) 10^{-6} \text{C}$	(0.227 ± 0.26) — 6
Hg ₂ Cl ₂ + Cl ⁻ = Hg + HgCl ₃ ⁻	$q_1 k_3 \kappa_2 k_0^{-1} = (1.2 \pm 0.5) 10^{-5}$	(0.08 ± 0.15) — 5
Hg ₂ Cl ₂ + 2Cl ⁻ = Hg + HgCl ₄ ²⁻	$q_2 k_3 \kappa_2 k_0^{-1} = (1.2 \pm 0.2) 10^{-4} \text{C}^{-1}$	(0.08 ± 0.06) — 4

In Table 4 is given a survey of the equilibrium constants that have been obtained directly by our measurements or that can be calculated from them by

means of, for example, the formulae in Part IV. In the second column is indicated how the other constants are calculated from the primary values: k_{12} , κ_2 , q_1, q_2 , k_s , and k_0 . Previous measurements by other workers have been quoted in the text.

SUMMARY

By electrometric measurements, a number of equilibrium constants, involving Hg^{2+} , HgCl^+ , HgCl_2 , HgCl_3^- , HgCl_4^{2-} , Hg_2^{2+} , $\text{Hg}_2\text{Cl}_2(\text{s})$, and $\text{Hg}(\text{l})$ have been determined. The constants are listed in Table 4. They are valid for the special experimental conditions: 25°C , $(\text{H}^+) = 10\text{ mC}$, ionic strength 500 mC .

At the beginning of this investigation Inger Brattsten, *leg. apot.*, carried out a large amount of pioneer work, which has proved of great value in this investigation and others to follow. We also wish to thank Mr. Erik Ekedahl, Mr. Gunnar Infeldt and Miss Ingegerd Qvarfort for their valuable aid.

REFERENCES

1. Sillén, L. G. *Svensk Kem. Tid.* **58** (1946) 52 (Part I).
2. Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 473 (Part IV).
3. Sillén, L. G., and Infeldt, G. *Svensk Kem. Tid.* **58** (1946) 61 (Part II).
4. Jonsson, A., Qvarfort, I., and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 461 (Part III).
5. Luther, R. *Z. physik. Chem.* **36** (1901) 402.
6. Morse, H. *Z. physik. Chem.* **41** (1902) 709.
7. Sherrill, M. S. *Z. physik. Chem.* **43** (1903) 705, see also **47** (1904) 103.
8. Buttle, B. H., and Hewitt, J. T. *J. Chem. Soc.* **93** (1908) 1405.
9. Drucker, K. *Z. Elektrochem.* **18** (1912) 236.
10. Carter, S. R., and Robinson, R. A. *J. Chem. Soc.* (1927) 1912.
11. Linhart, G. A. *J. Am. Chem. Soc.* **37** (1915) 258.
12. Sand, J., and Breest, F. *Z. physik. Chem.* **59** (1907) 428.
13. Linhart, G. A. *J. Am. Chem. Soc.* **38** (1916) 1272.
14. Job, P. *Ann. chim.* [10] **9** (1928) 156.
15. Garrett, A. B. *J. Am. Chem. Soc.* **61** (1939) 2744.

Received May 10, 1947.