Studies on the Hydrolysis of Metal Ions

III. The Hydrolysis of the Mercury (I) Ion, Hg_2^{2+}

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There are very few data in literature that might allow an estimation of the acidity of the ion Hg_2^{2+}. In 1904 Ley and Heimbucher[1] calculated $[H^+] = 3.42 \cdot 10^{-3}$ C from the velocity of sucrose inversion in 0.05 C $Hg_2(ClO_4)_2$ at 25° C, from which figure one may calculate $pk_{a1} = 3.6$, assuming Hg_2OH^+ to be the only product formed. Newbery[2] measured in 1936 the pH of mercury (I) perchlorate solutions with a glass electrode (temperature not stated), and from these data calculated values for pk_{a1} between 4.0 and 4.6.

For the sake of completeness it should be added that Guiter[3] measured the pH of mercury (I) nitrate solutions of various concentrations c, using a glass electrode. The accuracy seems to have been ± 0.1 or 0.05 pH units. From the variation of pH with $\log c$ he concluded that the predominant complex formed is $Hg_2OH(NO_3)_n^{-(n-1)}$ in the range 0.032—0.15 mC ($n = 9$ or 10), $(Hg_2OH)_n^{n+}$ in the range $c = 0.15$—65 mC ($n = 2$ or 3), and Hg_2OHNO_3 in the range 65—260 mC. Like many other of Guiter's results, this seems to conflict with the law of mass action. If the complexes with several nitrate groups, or those containing several Hg_2 groups, were to predominate even at low concentrations, their relative amounts would certainly be more likely to increase with increasing c.

There is one disturbing factor which does not seem to have been discussed in the earlier work quoted. Mercury (I) perchlorate or nitrate solutions as usually prepared generally contain about 1 % of mercury (II) ions, corresponding to the equilibrium $Hg^{2+} + Hg$ (1) $\rightleftharpoons Hg_2^{2+}$, the equilibrium constant of which is about 130[4,11]. Now Hg^{2+} is a rather strong acid ($pk_{a1} = 3.70$, $pk_{a2} = 2.60$, for 25° C and 0.5 C ClO_4^- as shown in part II), so that a large part of the observed acidity of mercury (I) solutions may be due to the mercury (II)

present. As will be shown below, this really accounts for the greater part of the observed acidity. However, there is a residual term due to mercury (I) acidity; but the acidity constant of mercury (I) is smaller than has previously been assumed.
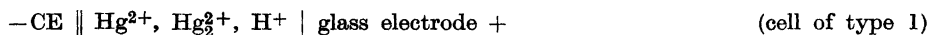
The work on mercury (I) and mercury (II) was carried out parallel because the constants for one ion were needed for calculating those of the other. Actually, the work on mercury (I) was started before that on mercury (II).

Choice of method and experimental conditions. For the same reasons as in Part I it was decided to study the equilibria at 25.0° C, using solutions with $[ClO_4^-] = 0.5$ C.

From the analysis of our solutions we might calculate the total concentration a of mercury (I) and mercury (II), and H, the value the hydrogen ion concentration would have had, if the mercury ions were not hydrolysed. In addition it was thought desirable to measure both the actual concentrations $[Hg_2^{2+}]$ and $[H^+]$ ($= h$).

The hydrogen ion concentration must be measured with a glass electrode, since both a hydrogen electrode and a quinhydrone electrode would have reduced the solutions, with the formation of metallic mercury.

The concentration of Hg_2^{2+} was measured with a mercury electrode. The same reference calomel electrode was used as in part II, CE $\|$ = Hg, Hg$_2$Cl$_2$ $|$ 4 C NaCl $|$ 0.5 C NaClO$_4$ $|$. Cells of the following types were thus used:

    $-$CE $\|$ Hg^{2+}, Hg$_2^{2+}$, H$^+$ $|$ glass electrode $+$ (cell of type 1)

    $-$CE $\|$ Hg^{2+}, Hg$_2^{2+}$, H$^+$ $|$ Hg $+$ (cell of type 3)

Cells of type 1 may be used for calculating the hydrogen ion concentration h in the same way as described in Part I. For cells of type 3 we have

$$E_3 = E_{03} + E_j + 29.58 \log [Hg_2^{2+}] \tag{1}$$

Here E_{03} is a constant, which is at first unknown, and E_j was taken to be $E_j = -0.0972\ h$ mV (h in mC) from preliminary work of Biedermann and Sillén [6].

<div align="center">EXPERIMENTS</div>

The *reagents* were prepared and analysed as described in Part I. The *apparatus* for titrating and measuring the emfs was also the same as in Part I. For cells of type 3, a mercury pool on the bottom of the titration vessel was used, into which a short platinum needle was dipped. The calomel electrode and salt bridge will be described below in some detail.

The *procedure* was the same as in Part I. First an acid-base titration was carried out with a glass electrode (cell of type 1), adding an alkaline solution T to an acid solution S_1. These solutions were free from mercury ions. Then a certain amount of a mercury (I) solution S_2 was added, mercury metal was introduced into the titration vessel, the platinum needle was inserted, and in the latter part of the titration both the CE-mercury cell (E_3) and the CE-glass electrode cell (E_1) were measured. A survey of the titrations is given in Table 1.

Table 1. Survey of the titrations.

No.	Symbol	S_1		T	S_2			ml added		
		a mC	mC H⁺	mC OH⁻	a mC	mC H⁺	S_1	T	S_2	S_2 + T
1	▲	2.00	40.00	40.06	4.00	10.46	40	39	79	27 + 27
2	□	0.50	40.00	40.08	1.00	10.00	40	39	79	25 + 25
3	◆	0.50	40.00	40.08	1.00	10.00	40	39	79	26 + 26
4	△	0.50	40.00	40.05	1.00	10.00	40	39	79	25 + 25
5	■	0.50	40.00	40.07	1.00	10.00	40	39	79	25.5 + 25.5
6	○	0.20	40.00	40.05	0.60	10.07	39.5	38.5	39	5.8 + 11.6
7	●	0.20	40.00	40.05	0.60	10.07	39.5	39	39.25	5.1 + 10.2
8	◑	0.20	40.00	40.07	0.40	10.00	40	39	79	26.5 + 26.5

Calomel electrode and salt bridge. Fig. 1 shows the calomel electrode and salt bridge with the stopcocks C_1—C_5, and the standard ground-glass joints J_1 and J_2. The apparatus is bent at right angles around the vertical lines through C_1 and C_3, so that seen from above it appears as on the lower right in Fig. 1. This is just to save space in our thermostats and has nothing to do with its function.

To the left of the three-way stopcock C_2 the apparatus is filled with 4 C NaCl, to the right of C_2 there is 0.5 C $NaClO_4$; this solution extends to the little bent capillary in the titration vessel to the right. The arrangement of the titration vessel has been described elsewhere [7]. The solution in it also contains 0.5 C ClO_4^-.

On the left in Fig. 1 is the electrode vessel with Hg and Hg_2Cl_2. A platinum needle dips into the mercury; there is a constriction at the lower end of the vessel in order to prevent aqueous solution from reaching the Pt needle at least with moderate movements of the electrode vessel.

In Fig. 1 the apparatus is shown as set up for a titration. The liquid junction at C_2 may be renewed at will by flushing alternately with NaCl and $NaClO_4$ solutions by suitable movements of C_1, C_3, and the three-way C_2. This was done before each titration, and sometimes in the middle of a titration. However, this operation never seemed to change the E of the cell, showing that the liquid junction potential at C_2 may be considered as constant.

Table 2 a. Data from titration no 3. Acid-base titration, initially 40.00 ml S_1 (40.00 mC H^+). T (40.08 mC OH^-) was added.

T ml	E_1 mV	$H = h$ mC	$E_{10} + E_d^*$ mV
9.00	+ 4.8	25.29	−78.2
12.00	+ 0.9	21.52	−77.9
17.00	− 5.1	16.11	−76.5
22.00	−13.4	11.58	−76.3
29.00	−28.2	6.343	−75.7
35.00	−49.9	2.629	−74.7
39.00	−92.5	0.4668	−72.9

Table 2 b. Mercury titration. Initially 79.00 ml S_2 (10.00 mC H^+, a = 1.00 mC) was added to the last solution from Table 2 a. For each volume of S_2, an equal volume of T was added.

T ml	H mC	E_1 mV	h mC	E_3 mV	δE mV
0.00	5.23	−32.8	5.21	428.20	
4.00	4.26	−37.8	4.25	428.00	
7.00	3.58	−42.0	3.60	428.10	0.05
12.00	2.56	−50.9	2.52	428.27	−0.01
16.02	1.81	−59.5	1.80	428.32	0.01
19.06	1.29	−68.0	1.29	428.42	−0.04
20.10	1.12	−71.9	1.10	428.31	0.08
21.00	0.98	−74.8	0.99	428.25	0.15
23.00	0.65	−84.6	0.67	428.23	0.21
24.00	0.51	−90.9	0.53	428.06	0.39
25.00	0.36	−98.9	0.38	427.87	0.59
26.00	0.21	−107.7	0.27	427.52	0.95

The emf was measured with C_5 open.

After a titration C_5 is closed, C_4 is opened, and C_2 is set so that $NaClO_4$ solution can be pressed out to the waste until its level reaches J_2. C_2 is closed, J_2 is disconnected, and a ground-glass stopper put into its she-joint. The apparatus to the left of J_2 is then kept in the thermostat. The part with C_4 and C_5 is emptied, washed, and dried.

At the onset of a new experiment, the tube to the right of C_5 is filled with $NaClO_4$ solution, which also extends about 1 cm to the left of C_5. C_5 is closed, the he-joint and she-joint of J_2 connected (the stopper having first been removed), and C_3 and C_4 opened so that the $NaClO_4$ solution fills the whole tube up to a few mm from C_4. Then C_3 and C_4 are closed.

Fig. 1. Cell with calomel electrode, salt bridge and titration vessels. In the latter a glass electrode and a Pt electrode have been inserted. (Burettes, nitrogen inlet, etc. are not shown.) a-d stopcock C_2 in different positions. On the lower right: cell seen from above. For details see text.
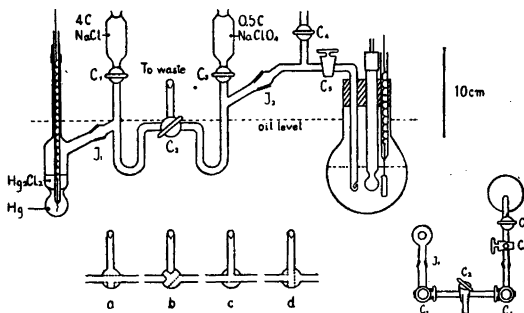
When it is desired to clean the part between J_1 and J_2, J_1 may be disconnected and a stopper put into the she-part of J_1. The calomel electrode can be kept in the thermostat bath all the time.

This apparatus is easily handled and in comparison with that used previously has the advantage that all sorts of operations can be performed without taking the calomel electrode out of the thermostat bath. The level of the oil bath is indicated in Fig. 1.
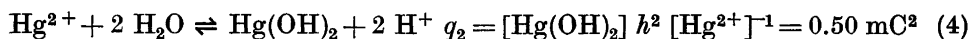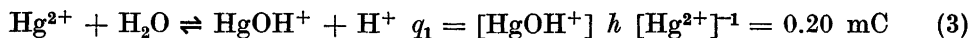
CALCULATIONS

The whole effect to be measured was very small. The calculations were chiefly founded on the measurements with the mercury electrode, which were rather accurate. The glass electrode was used for measuring

$$[\text{H}^+] = h \tag{2}$$

However, the quantity $H-h$, the hydrogen ion concentration set free by the hydrolysis processes, could not be obtained accurately enough from the glass electrode and analytical data to be used in the calculations.

It has been shown by Jonsson, Qvarfort, and Sillén [4] that a Hg electrode in a solution containing Hg_2^{2+} and Hg^{2+} ions quickly acquires the potential corresponding to the final equilibrium between the solution and Hg metal. We may thus assume that this equilibrium had been established in the solution.

From Part I we take the equilibrium constants

$$\text{Hg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{HgOH}^+ + \text{H}^+ \quad q_1 = [\text{HgOH}^+]\, h\, [\text{Hg}^{2+}]^{-1} = 0.20 \text{ mC} \tag{3}$$

$$\text{Hg}^{2+} + 2\,\text{H}_2\text{O} \rightleftharpoons \text{Hg(OH)}_2 + 2\,\text{H}^+ \quad q_2 = [\text{Hg(OH)}_2]\, h^2\, [\text{Hg}^{2+}]^{-1} = 0.50 \text{ mC}^2 \tag{4}$$

The work of Jonsson, Qvarfort and Sillén was carried out with $h = 10$ mC; with this acidity the hydrolysis of Hg_2^{2+} may be neglected, but a correction

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should be made for that of Hg^{2+}. We take from their paper that at equilibrium for $[H^+] = 10$ mC

$$[Hg_2^{2+}][Hg^{II}]_{tot}^{-1} = 129.2 \pm 1.0 \qquad (5)$$
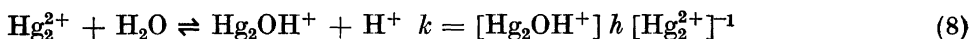
Using (3), (4) and (9, Part I):

$$129.2 \pm 1.0 = [Hg_2^{2+}][Hg^{2+}]^{-1}(1 + q_1h^{-1} + q_2h^{-2})^{-1} = [Hg_2^{2+}][Hg^{2+}]^{-1} \cdot 1.025^{-1} \quad (6)$$

Thus we find the real equilibrium constant

$$Hg^{2+} + Hg(l) \rightleftharpoons Hg_2^{2+} \quad k_0 = [Hg_2^{2+}][Hg^{2+}]^{-1} = 132.4 \pm 1.0 \qquad (7)$$

Since the hydrolysis of the Hg_2^{2+} ions is a very small effect, the best thing we can do is probably to make the simplest assumption, namely that the only product is Hg_2OH^+, so that the reaction is

$$Hg_2^{2+} + H_2O \rightleftharpoons Hg_2OH^+ + H^+ \quad k = [Hg_2OH^+] \, h \, [Hg_2^{2+}]^{-1} \qquad (8)$$

From the analytical data we know the total mercury ion concentration a

$$a = [Hg_2^{2+}] + [Hg_2OH^+] + [Hg^{2+}] + [HgOH^+] + [Hg(OH)_2] \qquad (9)$$

From the equilibrium conditions (3), (4), (7), and (8) we deduce

$$a = [Hg_2^{2+}] \, (1 + kh^{-1} + k_0^{-1}(1 + q_1h^{-1} + q_2h^{-2})) = [Hg_2^{2+}] \, (1 + \psi) \qquad (10)$$

By introducing (10) we may transform the expression (2) for E_3

$$E_3 = E_{03} + E_j + 29.58 \log a - 29.58 \log (1 + \psi) \qquad (11)$$

Now let us consider the fixed value $h' = 10^{0.5}$ mC $= 10^{-2.5}$ C and denote the values for E_3 and ψ at this point by E_3' and ψ'. Then we have

$$E_3' = E_{03} + 29.58 \log a - 29.58 \log (1 + \psi') + E_j' \qquad (12)$$

We shall now define the quantity

$$\delta E = E_3' - E_j' - (E_3 - E_j) = E_3' - E_3 + 0.0972(h' - h) =$$
$$= 29.58 \, [\log(1 + \psi) - \log(1 + \psi')] \qquad (13)$$

Fig. 2. gives δE as a function of $\log h$. The experimental points have been calculated from the measured E_3 by means of (13). They are uncertain by several 0.01 mV depending on how E_3' is calculated. The curves have been calculated from the right member of (13) using the expression for ψ from (10)

$$\psi = kh^{-1} + k_0^{-1} \, (1 + q_1h^{-1} + q_2h^{-2}) \qquad (14)$$

The values for q_1, q_2, and k_0 were taken from (3), (4), and (7), and different values for k were tried.
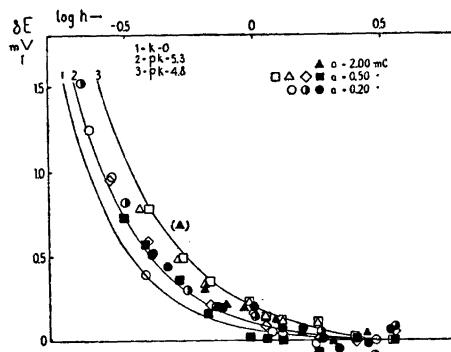
Fig. 2. δE *in* mV *as a function of* $\log h$ *(h in mC). Experimental points: symbols see Table 1. Curves calculated for different values of* k. *Curve 1 gives the effect of* Hg^{2+}, *provided* Hg_2^{2+} *is not at all acid (k = 0).*

As is seen from the curve $k = 0$ (no hydrolysis of Hg_2^{2+}), the greatest part of δE is explained by the hydrolysis of Hg^{2+}. However, the experimental points are consistently slightly above the curve for $k = 0$, thus showing that there is in addition a small hydrolysis of Hg_2^{2+}. Because of the smallness of the effect, the equilibrium cannot be studied very exactly. However, assuming that Hg_2OH^+ is the chief product, one may estimate the acid constant to be within the range

$$k = [Hg_2OH^+] \ h \ [Hg_2^{2+}]^{-1} = 10^{-5.0 \pm 0.3} \ C \qquad (15)$$

This value is smaller than those obtained in previous investigations [1,2].

One might argue that the hydrogen ion concentration has been measured in the bulk of the solution and thus does not correspond to the final equilibrium with mercury metal. However, much more weight has been put in the calculations on the values of E_3 (mercury electrode) than on those of E_1 (glass electrode). In Fig. 2, for instance, 1 mV in the mercury electrode scale corresponds to almost 40 mV in the glass electrode scale. Since the mercury (I) solution has previously been equilibrated with mercury, it cannot be far from the new equilibrium, so the error in h should be small.

STANDARD POTENTIALS

The work of our team on mercury complexes has hitherto been concerned with emfs and equilibria with solutions containing 0.5 C ClO_4^- at 25° C, and not with the constants for infinitely dilute solutions. However, we shall attempt a few remarks on the standard potentials. The standard potentials e_{10}^0 for $Hg_2^{2+} \mid Hg$ and e_{21}^0 for $Hg_2^{2+}, Hg^{2+} \mid Pt$ are related to the equilibrium constant K_0 for infinite dilution for the reaction

$$Hg^{2+} + Hg(l) \rightleftharpoons Hg_2^{2+} \quad K_0 = [Hg_2^{2+}][Hg^{2+}]^{-1} \qquad (16)$$
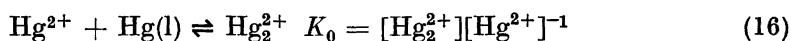
by the relation, for 25° C

$$e_{21}^0 - e_{10}^0 = 59.16 \log K_0 \tag{17}$$

The accepted values for the standard potentials have been determined from emf measurements by extrapolation to infinite dilution, to eliminate the activity factors. However, with increasing dilution the hydrolysis of the ions causes an increasing error, which will be especially great for e_{21}^0, since Hg^{2+} is a rather strong acid. This error will tend to make e_{21}^0 too low.

On the other hand, the constant K_0 contains the ratio of the activity factors of two dipositive ions which may be expected to be not far from unity even at considerable ionic strengths. Thus the concentration ratios measured at ionic strengths around 0.5 C may be good approximations for K_0, provided the solution is sufficiently acid.

We conclude that of the three quantities in (17), K_0 and e_{10}^0 can be most reliably determined, whereas e_{21}^0 should preferably be calculated from the other two than determined separately by the very uncertain extrapolation method.

For e_{10}^0 Linhart's measurements [8] at 25° C have been recalculated by Lewis and Randall, and by Bray and Hershey [10]. They found + 798.6 mV, and + 797.5 $\pm$ 1.0 mV.

Let us assume

$$Hg_2^{2+} \mid Hg \qquad e_{10}^0 = 798 \pm 1 \text{ mV} \tag{18}$$

For K_0 we have Abel's measurements [11] which give the equilibrium ratio $[Hg_2^{2+}]_{tot}[Hg^{2+}]_{tot}^{-1} = 119.8$ at 25° C in about 0.3 C HNO_3. Now Hg^{2+} forms complexes with NO_3^- a little more readily than Hg_2^{2+}. Using Infeldt's and Sillén's values [12] for the equilibrium constants (although these are really valid for $[ClO_4^-] = 3$ C) we find that for 0.3 C NO_3^-, $[Hg^{2+}]_{tot} = [Hg^{2+}] \cdot 1.47_4$, and $[Hg_2^{2+}]_{tot} = [Hg_2^{2+}] \cdot 1.36$, which gives the ratio of the free ions $[Hg_2^{2+}]$ $[Hg^{2+}]^{-1} = 119.8 \cdot 1.47 \cdot 1.36^{-1} = 130$, which agrees well with the ratio 132.4 found in (7) for 0.5 C ClO_4^-. Since the activity factors should approximately cancel each other, we may assume for infinite dilution

$$Hg^{2+} + Hg(l) \rightleftharpoons Hg_2^{2+} \qquad K_0 = 130 \pm 10 \tag{19}$$

thus from (17)

$$e_{21}^0 - e_{10}^0 = 125 \pm 2 \text{ mV} \tag{20}$$

which gives, provided (18) is correct

$$Hg^{2+}, Hg_2^{2+} \mid Pt \; e_{21}^0 = + 923 \pm 3 \text{ mV} \tag{21}$$

SUMMARY

The hydrolysis of the mercury (I) ion Hg_2^{2+} has been studied at 25.0° C and $[ClO_4^-] = 0.5$ C. The acidity of mercury (I) salt solutions, which has previously been ascribed to the acidity of Hg_2^{2+}, has proved to be chiefly due to the acidity of Hg^{2+}, which is always present in small amounts and is a rather strong acid. A small residual effect must be ascribed to the acidity of Hg_2^{2+}; the pk_a is estimated at 5.0 ± 0.3, which means that Hg_2^{2+} is a weaker acid than has previously been assumed.

The standard potential e_{21}^0 for Hg^{2+}, Hg_2^{2+} | Pt should preferably be calculated from measured values of the standard potential e_{10}^0 for Hg_2^{2+} | Hg and the equilibrium constant K_0 for $Hg^{2+} + Hg(l) \rightleftharpoons Hg_2^{2+}$, than from direct measurements. Taking as best literature data $e_{10}^0 = 798 \pm 1$ mV and $K_0 = 130 \pm 10$ one finds $e_{21}^0 = 923 \pm 3$ mV, which is higher than the usually accepted value.

This is in good accord with the value 0.92 V given by Abegg, Auerbach, and Luther in 1911 [13] (they gave 0.80 V for e_{10}^0), but differs from later values: 905 mV [14] and 910 mV [15] obtained by an uncertain extrapolation of Popoff's values [14]. (Added in proof) Latimer ([14], 1952 edition) quotes $e_{10}^0 = 789$ mV from a New Zealand thesis of M. T. Christensen, which was not available to us. This would give $e_{21}^0 = 914$ mV.

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