

Thermochemical Studies of Hydrolytic Reactions

3. A Thermochemical Study of Hydrolysed $\text{Hg}(\text{ClO}_4)_2$ Solutions*

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The heats of formation of mercury(II)hydroxocomplexes in 3 M $(\text{Na})\text{ClO}_4$ at 25°C have been determined by means of enthalpy titrations of hydrolysed $\text{Hg}(\text{ClO}_4)_2$ solutions. Assuming the hydrolysis mechanism and equilibrium constants proposed by Ingrid Ahlberg,¹ the following results were obtained.

	ΔH , kcal	ΔS , e.u.
$\text{Hg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{HgOH}^+ + \text{H}^+$	7.23 ± 0.18	7.9 ± 0.7
$\text{Hg}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Hg}(\text{OH})_2 + 2\text{H}^+$	9.84 ± 0.16	4.6 ± 0.6
$2\text{Hg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Hg}_2(\text{OH})^{3+} + \text{H}^+$	3.06 ± 0.22	-2.1 ± 0.9
$2\text{Hg}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Hg}_2(\text{OH})_2^{2+} + 2\text{H}^+$	12.70 ± 0.45	18.8 ± 1.6

The hydrolysis of mercury(II) has been studied by Hietanen and Sillén² using 0.5 M $(\text{Na})\text{ClO}_4$ as ionic medium and Hg concentrations up to 0.015 M. They found in this range two mononuclear complexes, HgOH^+ and $\text{Hg}(\text{OH})_2$. In more concentrated $\text{Hg}(\text{ClO}_4)_2$ solutions Ingrid Ahlberg,¹ using 3 M $(\text{Na})\text{ClO}_4$ as ionic medium, found that polynuclear complexes also exist. She explained her emf data by assuming the complexes: HgOH^+ , $\text{Hg}(\text{OH})_2$, $\text{Hg}_2\text{OH}^{3+}$, $\text{Hg}_2(\text{OH})_2^{2+}$ (and $\text{Hg}_4(\text{OH})_5^{5+}$).

The second acidity constant of mercury(II) is larger than the first one, as was first observed by Hietanen and Sillén. This behavior of the mercury(II) ion as an acid differs from the behavior of many polybasic acids for which the second acidity constant is usually smaller than the first one by a factor of 10^{-5} . The present thermochemical investigation was undertaken primarily in order to obtain information about the enthalpy and entropy terms for the dissociation of the first and second proton from the mercury(II) ion.

As far as we know no thermochemical data for hydrolysed mercury(II) solutions are given in literature.

* Part 1 = Ref. 13. Part 2 = Ref. 14.

EXPERIMENTAL

The calorimetric technique used in this work is the one developed by Sillén and Schlyter.^{3,4} The calorimeter described by Schlyter⁴ has, however, been modified in many respects. The calorimeter, which is shown in Fig. 1, now consists of an outer, chrome-plated brass can with lid and sleeve, with an O-ring seal between the lid and the can (this part of the calorimeter closely resembles the calorimeter described by Gerding, Leden, and Sunner⁵), and an inner glass vessel (300 ml beaker) directly connected to the outer lid by means of a threaded brass ring. The outer calorimeter can is wholly immersed in a large constant temperature bath maintained at $25.000 \pm 0.003^\circ\text{C}$.

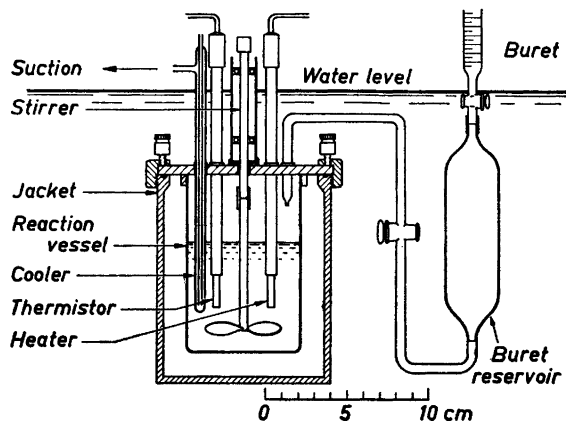


Fig. 1. Calorimeter.

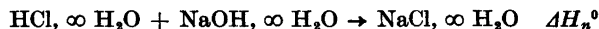
The experiments consist of titrations in which successive additions of v ml of a solution T are made to V_0 ml ($V_0 = 224.53$ ml) of a solution S contained in the calorimeter. The additions of T are made with a buret provided with a bulb, which is also immersed in the water thermostat so that the added solution has practically the same temperature as the thermostat.

The calorimeter vessel contains the tip of the buret, a stirrer, a heater, a thermistor, and a glass coil for cooling with cold air. The heater and thermistor are contained in glass tubes at the end of which are sealed gold thimbles.

A conventional DC-Wheatstone bridge is used to measure the resistance of the 5000 ohm thermistor (Stantel). A stabilized DC Microvolt Amplifier (Leeds and Northrup No. 9835 B) is used as a null instrument. The smallest detectable temperature difference is about 3×10^{-5} degrees, corresponding to ± 0.01 cal.

Before each addition of T, the temperature inside the calorimeter vessel is adjusted by means of the air cooler and the heating coil so that it is as close as possible to the temperature of the water thermostat and thus of T.

The calorimeter was occasionally tested by neutralization of 0.1 M NaOH with 0.1 M HCl. By use of the known heats of dilution of HCl, NaOH, and NaCl,⁶ we obtained for the reaction

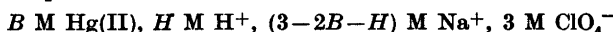


$\Delta H_n^\circ = -13.30, -13.30$ and -13.35 kcal/mole as the result of three different titrations. (The correction of the results to infinite dilution was of the order of 0.2 kcal/mole.) This is, for our purpose, in sufficiently good agreement with the value $\Delta H_n^\circ = -13.34$ kcal/mole, well established in the literature.^{5,7}

The hydrolysed mercury perchlorate solutions were prepared by dissolving a slight excess of mercury(II)oxide (Merck *p.a.*) in a known amount of standard perchloric acid (Kebo *p.a.*). The solution was left overnight with continuous stirring. After addition of perchlorate and dilution to the desired volume the small excess of HgO was filtered off through a porcelain filter, on which was placed a thin layer of filter paper pulp ("Whatman ashless tablet"). The concentration of mercury, B , in the solution was determined by Winkler's method,⁸ in which Hg is precipitated as Hg_2Cl_2 . The analytical hydrogen ion excess, H_s , was calculated from $H_s = [ClO_4^-] - 2B$, where $[ClO_4^-]$ is known from the amount of standard perchloric acid used for the dissolution of the oxide.

The acid solutions were made simply by dissolving a weighed amount of HgO in a known excess of standard perchloric acid.

The general composition of the solutions S and T was:



The values for B , the total Hg(II) concentration, and H , the analytical hydrogen excess, for the different titrations are given in Table 1.

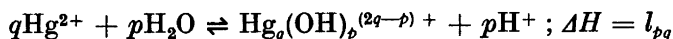
A total of 21 enthalpy titrations were performed, giving 144 titration points. The total heat evolved per titration varied between 1.4 and 11.2 cal. The heat effect per addition from the buret varied between 0.1 and 2.5 cal.

Table 1. Survey of titrations.

	Titration No.							
	1a, b, c	2a, b	3a, b	4a, b, c	5a, b, c	6a, b, c, d	7a, b, c	8
B_s , M	0.00201	0.00479	0.00937	0.02458	0.04931	0.1000	0.1500	0.2000
B_T , M	0.00250	0.00500	0.01000	0.02500	0.05000	0.1000	0.1500	0.2000
H_s , M	-0.00145	-0.00062	0.00225	0.00084	0.00138	0.00	0.00	0.00
H_T , M	0.1111	0.1061	0.1100	0.2000	0.3000	0.4500	0.4500	0.5000

RESULTS AND CALCULATIONS

The reactions we have been studying can be written



ΔH for this reaction may be called the relative molar enthalpy l_{pq} of the complex $Hg_q(OH)_p^{(2q-p)+}$ and its equilibrium constant will be called β_{pq} . The values for the β_{pq} were taken from the emf work of Ahlberg:¹ $\log \beta_{11} = -3.56 \pm 0.08$, $\log \beta_{21} = -6.21 \pm 0.02$, $\log \beta_{12} = -2.7 \pm 0.1$, and $\log \beta_{22} = -5.2 \pm 0.1$.

After an addition of v ml of the acid solution T to the initial volume of the hydrolysed solution S, V_0 ml, the total excess enthalpy, L , in the calorimeter may be defined as

$$L = V \sum c_{pq} \cdot l_{pq}$$

where c_{pq} is the concentration of $Hg_q(OH)_p^{(2q-p)+}$ and $V = V_0 + v$.

If L' and V' are the excess enthalpy and volume before an addition from the buret and L'' and V'' after the addition the heat evolved is

$$Q = L' - L'' + (V'' - V') l_T$$

where l_T (cal/l) is the excess enthalpy of solution T ("heat of dilution"). However, measurements showed that l_T is quite negligible.

Pairs of (Q, v) values are obtained as results of an enthalpy titration. To find the "best" values for the unknown l_{pq} we have used the calorimeter version of the least squares computer program LETAGROPVRID^{9,10} using a UNIVAC 1107 computer. With the program LETAGROPVRID the computer searches for the set of values of the unknown parameters, k_i , which will minimize the error square sum

$$U = \sum(Q_{\text{calc}} - Q)^2$$

The input information used with the program in our case is the equilibrium constants β_{pq} and estimates of the enthalpies l_{pq} (common for all data), B_s , B_T , H_s , H_T , and V_0 (for each titration), v and Q (for each point).

The output information is a set of l_{pq} with their standard deviations and the standard deviation in the Q measurements (σ_Q).

In addition we assumed that in each titration there is a small analytical error, δH_s , in the determination of H_s for the first solution. These systematic errors δH_s were also treated as unknown constants to be determined.

From seven titrations with $B \leq 0.010$ M it was possible to determine the enthalpies l_{11} and l_{21} for the two mononuclear reactions. Polynuclear complexes do not appear in appreciable amounts at these low metal concentrations.

We obtained

$$\begin{aligned} l_{11} &= 7.2 \pm 0.4 \text{ kcal/mole} \\ l_{21} &= 9.6 \pm 0.2 \quad \text{»} \end{aligned}$$

with $\sigma_Q = 0.028$ cal

When the data from all the 21 titrations, with B values from 0.0025 up to 0.2 M, were treated together we obtained the following values:

$$\begin{aligned} l_{11} &= 7.23 \pm 0.18 \text{ kcal/mole} \\ l_{21} &= 9.84 \pm 0.16 \quad \text{»} \\ l_{12} &= 3.06 \pm 0.22 \quad \text{»} \\ l_{22} &= 12.70 \pm 0.45 \quad \text{»} \end{aligned}$$

with $\sigma_Q = 0.033$ cal.

The deviations given are σ , the standard deviation calculated by LETAGROPVRID.

To explain certain deviations at high B values, Ahlberg suggested a complex $\text{Hg}_4(\text{OH})_3^{5+}$. However, this complex need not be taken into account at the B values used by us.

With the enthalpies calculated above we got a good agreement between the measured and calculated Q -values over the whole concentration range investigated, with no systematic deviation in any region. This gives a certain support to the hydrolysis mechanism proposed by Ahlberg. The comparatively high uncertainty of l_{22} might be expected, as the complex $\text{Hg}_2(\text{OH})_2^{2+}$ never dominates in the solutions.

In Table 2 are given the experimental data, $[v[\text{ml}], Q[\text{cal}]]$, together with the deviation between the calculated and measured heat, $(Q_{\text{calc}} - Q)[\text{cal}]$.

Table 2. Survey of measurements. Values of v [ml], Q [cal], $(Q_{\text{calc}} - Q)$ [cal].

Titr. 1a. $B_s = 2.01$ mM, $H_s = -1.45$ mM, $\delta H_s = (0.00 \pm 0.07)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 1.97, 0.67, 0.02; 5.97, 1.01, -0.01; 9.96, 0.40, 0.01; 14.97, 0.15, 0.02; 19.96, 0.04, 0.03.

Titr. 1b. $B_s = 2.01$ mM, $H_s = -1.45$ mM, $\delta H_s = (0.06 \pm 0.03)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 3.00, 0.99, 0.00; 7.00, 0.80, 0.00; 11.00, 0.30, 0.01; 16.00, 0.17, -0.02; 21.00, 0.07, -0.01.

Titr. 1c. $B_s = 2.01$ mM, $H_s = -1.45$ mM, $\delta H_s = (0.00 \pm 0.03)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 1.00, 0.37, 0.00; 3.98, 0.91, 0.00; 7.98, 0.66, 0.01; 12.98, 0.30, 0.00; 17.97, 0.09, 0.00.

Titr. 2a. $B_s = 4.79$ mM, $H_s = -0.62$ mM, $\delta H_s = (0.21 \pm 0.05)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 3.00, 0.85, 0.00; 5.00, 0.41, 0.00; 7.00, 0.34, -0.04; 11.00, 0.34, 0.02; 15.00, 0.19, 0.00; 20.00, 0.11, 0.01.

Titr. 2b. $B_s = 4.79$ mM, $H_s = -0.62$ mM, $\delta H_s = (0.22 \pm 0.03)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 3.00, 0.86, -0.03; 5.00, 0.41, 0.00; 7.00, 0.32, -0.02; 11.00, 0.33, 0.02; 15.00, 0.17, 0.01; 20.00, 0.12, 0.00.

Titr. 3a. $B_s = 9.37$ mM, $H_s = 2.25$ mM, $\delta H_s = (0.00 \pm 0.05)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 2.00, 0.35, 0.00; 4.00, 0.28, -0.01; 6.00, 0.20, 0.00; 10.00, 0.24, 0.02; 15.00, 0.18, 0.01; 20.00, 0.13, -0.01.

Titr. 3b. $B_s = 9.37$ mM, $H_s = 2.25$ mM, $\delta H_s = -(0.14 \pm 0.15)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 3.00, 0.55, -0.03; 5.00, 0.24, 0.00; 8.00, 0.25, 0.00; 12.00, 0.21, 0.01; 16.00, 0.11, 0.02; 20.00, 0.08, 0.01.

Titr. 4a. $B_s = 24.58$ mM, $H_s = 0.84$ mM, $\delta H_s = (0.00 \pm 0.12)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 2.00, 0.98, 0.01; 4.00, 0.73, 0.01; 6.00, 0.52, 0.03; 8.00, 0.43, -0.03; 12.05, 0.56, -0.05; 16.00, 0.26, 0.01; 20.00, 0.16, 0.02.

Titr. 4b. $B_s = 24.58$ mM, $H_s = 0.84$ mM, $\delta H_s = (0.11 \pm 0.14)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 1.00, 0.53, 0.00; 3.00, 0.88, -0.02; 5.00, 0.62, 0.00; 7.00, 0.45, 0.00; 9.00, 0.36, -0.02; 13.00, 0.44, -0.01; 20.00, 0.31, 0.07.

Titr. 4c. $B_s = 24.58$ mM, $H_s = 0.84$ mM, $\delta H_s = (0.27 \pm 0.14)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 3.00, 1.35, -0.01; 7.00, 1.07, -0.01; 11.00, 0.54, 0.01; 15.00, 0.31, 0.00; 20.00, 0.22, 0.01.

Titr. 5a. $B_s = 49.31$ mM, $H_s = 1.38$ mM, $\delta H_s = -(0.34 \pm 0.17)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 1.00, 0.77, 0.02; 3.00, 1.33, -0.03; 5.00, 0.97, -0.04; 7.00, 0.66, 0.00; 9.00, 0.44, 0.02; 12.00, 0.45, 0.02; 16.00, 0.34, 0.06; 20.00, 0.23, 0.02.

Titr. 5b. $B_s = 49.31$ mM, $H_s = 1.38$ mM, $\delta H_s = -(0.34 \pm 0.11)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 2.00, 1.48, 0.01; 4.00, 1.12, -0.02; 6.00, 0.80, -0.01; 8.00, 0.57, -0.01; 10.00, 0.40, 0.00; 13.00, 0.40, 0.01; 16.00, 0.28, 0.00; 20.00, 0.21, 0.04.

Titr. 5c. $B_s = 49.31$ mM, $H_s = 1.38$ mM, $\delta H_s = -(0.39 \pm 0.09)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 1.00, 0.80, 0.00; 3.00, 1.31, 0.00; 5.00, 0.93, 0.00; 7.00, 0.69, -0.02; 9.00, 0.47, 0.00; 12.00, 0.45, 0.02; 16.00, 0.40, 0.00; 20.00, 0.27, -0.01.

Titr. 6a. $B_s = 100.0$ mM, $H_s = 0.00$ mM, $\delta H_s = (0.06 \pm 0.16)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 1.00, 1.26, 0.00; 3.00, 2.08, -0.02; 5.00, 1.44, 0.04; 7.00, 1.12, -0.07; 9.00, 0.76, 0.00; 11.00, 0.54, 0.00; 15.00, 0.68, 0.03; 20.00, 0.46, 0.05.

Titr. 6b. $B_s = 100.0$ mM, $H_s = 0.00$ mM, $\delta H_s = (0.06 \pm 0.14)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 3.00, 3.29, 0.02; 5.00, 1.53, -0.04; 7.00, 1.11, -0.05; 10.00, 1.07, -0.02; 13.00, 0.63, 0.02; 16.00, 0.39, 0.05; 20.00, 0.36, 0.03.

Titr. 6c. $B_s = 100.0$ mM, $H_s = 0.00$ mM, $\delta H_s = (0.10 \pm 0.16)$ mM; $v, Q_{\text{calc}}, (Q - Q)$; 1.00, 1.22, 0.03; 3.00, 2.05, 0.00; 5.00, 1.52, -0.04; 7.00, 1.07, -0.02; 9.00, 0.76, -0.01; 11.00, 0.53, 0.01; 15.00, 0.68, 0.03; 20.00, 0.44, 0.07.

Tit. 6d. $B_s = 100.0$ mM, $H_s = 0.00$ mM, $\delta H_s = (0.00 \pm 0.17)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 2.00, 2.36, 0.01; 4.00, 1.85, -0.08; 6.00, 1.27, 0.00; 8.00, 0.87, 0.01; 12.00, 1.05, 0.05; 16.00, 0.60, 0.03; 20.00, 0.37, 0.01.

Tit. 7a. $B_s = 150.0$ mM, $H_s = 0.00$ mM, $\delta H_s = -(0.19 \pm 0.23)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 1.00, 1.15, 0.07; 3.00, 2.05, 0.04; 5.00, 1.66, -0.01; 7.00, 1.32, -0.04; 9.00, 1.04, -0.07; 11.00, 0.75, 0.00; 15.00, 1.08, -0.03; 20.00, 0.79, 0.01.

Tit. 7b. $B_s = 150.0$ mM, $H_s = 0.00$ mM, $\delta H_s = (0.31 \pm 0.26)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 2.00, 2.18, 0.09; 4.00, 1.86, -0.04; 6.00, 1.49, -0.09; 8.00, 1.11, -0.03; 12.00, 1.44, 0.02; 16.00, 0.89, 0.01; 20.00, 0.55, 0.03.

Tit. 7c. $B_s = 150.0$ mM, $H_s = 0.00$ mM, $\delta H_s = (0.09 \pm 0.15)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 2.00, 2.28, 0.02; 4.00, 1.82, 0.01; 6.00, 1.46, -0.03; 8.00, 1.13, -0.04; 10.00, 0.87, -0.03; 12.00, 0.66, -0.01; 16.00, 0.88, 0.03; 20.00, 0.56, 0.04.

Tit. 8. $B_s = 200.0$ mM, $H_s = 0.00$ mM, $\delta H_s = -(0.24 \pm 0.21)$ mM; $v, Q, (Q_{\text{calc}} - Q)$; 2.00, 2.46, 0.06; 4.00, 2.06, -0.01; 6.00, 1.66, -0.03; 8.00, 1.32, -0.05; 10.00, 1.04, -0.03; 12.00, 0.81, -0.01; 16.00, 1.08, 0.05; 20.00, 0.73, 0.03.

For each titration is also given the small correction, δH_s , to the analytical hydrogen excess H_s , estimated by the computer.

In Fig. 2 is plotted the cumulative heat, $\sum Q$, as a function of the added volume v , for one titration (No. 6c). The curve has been calculated assuming the l_{pq} above and the circles are experimental points. On the scale used in the diagram it is difficult to see small deviations in $\sum Q$. In Fig. 3 are given, for the same titration, the concentrations of the different complexes, c_{pq} , as a function of v .

The thermochemical data (ΔG from Ahlberg) are summarized in Table 3.

The heat of ionisation of water in 3 M NaClO_4 was determined by means of an enthalpy titration of ≈ 5 mM NaOH , prepared by electrolysis, with 0.1 M HClO_4 . The value obtained was 13.05 ± 0.03 kcal/mole, neglecting the probably very small dilution effects. From the value of $\log K_w = -14.22$ in 3 M NaClO_4 ,¹¹ we obtain $\Delta G = 19.40$ kcal/mole.

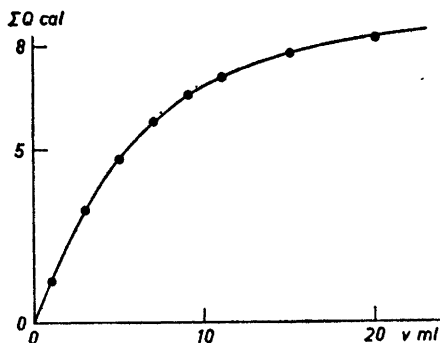


Fig. 2. The cumulative heat, $\sum Q$, as a function of the added volume v (titr. No. 6c). Circles: experimental values. Curve: calculated values.

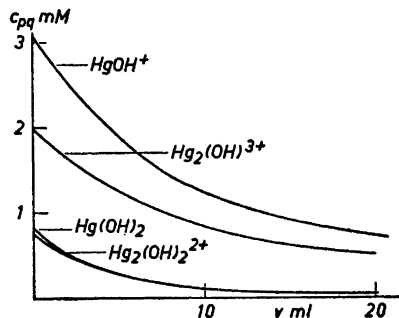
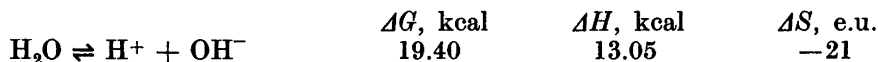


Fig. 3. The concentrations, c_{pq} , of the different complexes as a function of v (titr. No. 6c).

Combining the data in Table 3a with the thermochemical data for the ionisation of water in 3 M NaClO₄ medium



we obtain the thermochemical data in Table 3 b for the reactions written:

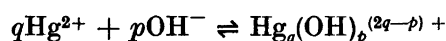


Table 3. Summary of thermochemical data.

Reaction	ΔG , kcal	ΔH , kcal	ΔS , e.u.
a)			
$\text{Hg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{HgOH}^+ + \text{H}^+$	4.86 ± 0.11	7.23 ± 0.18	7.95 ± 0.71
$\text{Hg}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Hg}(\text{OH})_2 + 2\text{H}^+$	8.47 ± 0.03	9.84 ± 0.16	4.59 ± 0.55
$2\text{Hg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Hg}_2(\text{OH})_2^{2+} + \text{H}^+$	3.68 ± 0.14	3.06 ± 0.22	-2.08 ± 0.88
$2\text{Hg}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Hg}_2(\text{OH})_2^{2+} + 2\text{H}^+$	7.09 ± 0.14	12.70 ± 0.45	18.8 ± 1.58
b)			
$\text{Hg}^{2+} + \text{OH}^+ \rightleftharpoons \text{HgOH}^+$	-14.5	-5.8	+29
$\text{Hg}^{2+} + 2\text{OH}^+ \rightleftharpoons \text{Hg}(\text{OH})_2$	-30.3	-16.3	+47
$2\text{Hg}^{2+} + \text{OH}^+ \rightleftharpoons \text{Hg}_2(\text{OH})_2^{2+}$	-15.7	-10.0	+19
$2\text{Hg}^{2+} + 2\text{OH}^+ \rightleftharpoons \text{Hg}_2(\text{OH})_2^{2+}$	-31.7	-13.4	+61
c)			
$\text{H}_2\text{OHgH}_2\text{O}^{2+} \rightleftharpoons \text{H}_2\text{OHgOH}^+ + \text{H}^+$	4.86 ± 0.11	7.23 ± 0.18	7.9 ± 0.7
$\text{H}_2\text{OHgOH}^+ \rightleftharpoons \text{HOHgOH} + \text{H}^+$	3.61 ± 0.11	2.61 ± 0.24	-3.4 ± 0.9
$2\text{HgOH}^+ \rightleftharpoons \text{Hg}(\text{OH})_2 + \text{Hg}^{2+}$	-1.25 ± 0.16	-4.62 ± 0.30	-11.3 ± 1.1

DISCUSSION

The thermochemical data for the dissociation of the first and the second proton from the diaquamercury(II) ion are given in Table 3 c.

As can be seen there is a difference in ΔH of about 5 kcal/mole between the splitting of the first and the second proton.

Table 4.

Reaction	ΔG , kcal	ΔH , kcal	ΔS , e.u.
$\text{Hg}^{2+} + \text{OH}^- \rightleftharpoons \text{HgOH}^+$	-14.5	-5.8	+29
$\text{Hg}^{2+} + \text{Cl}^- \rightleftharpoons \text{HgCl}^+$	-9.6	-5.8	+13
$\text{Hg}^{2+} + \text{Br}^- \rightleftharpoons \text{HgBr}^+$	-12.8	-9.6	+11
$\text{HgOH}^+ + \text{OH}^- \rightleftharpoons \text{Hg}(\text{OH})_2$	-15.8	-10.4	+18
$\text{HgCl}^+ + \text{Cl}^- \rightleftharpoons \text{HgCl}_2$	-9.4	-6.5	+10
$\text{HgBr}^+ + \text{Br}^- \rightleftharpoons \text{HgBr}_2$	-11.7	-9.6	+7

In Table 4 we have compared the thermochemical data for the reaction $\text{Hg}^{2+} + n\text{X}^- \rightleftharpoons \text{HgX}^{(2-n)+}$ ($n = 1, 2$) in 3 M NaClO₄ where $\text{X} = \text{OH}^-$, Cl^- , Br^- . Data for $\text{X} = \text{Cl}^-$, Br^- have been taken from an earlier work of Arnek.¹² From the comparison it is obvious that for $\text{X} = \text{Cl}^-$ and Br^- , ΔH

for the binding of the first and second ligand are roughly the same, whereas for $X = OH^-$ there is a difference, as stated above, of about 5 kcal/mole for the first and second step. One might suggest that two different kinds of processes are occurring when the first and second proton is split from the diaqua-mercury(II)ion. " $Hg(OH)_2$ " may, e.g., be an oxocomplex $HgO(H_2O)_n$, like $VO(H_2O)_5^{2+}$. This should mean that the first proton is split from H_2O bound to mercury and the second proton is split from OH bound to mercury.

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REFERENCES

1. Ahlberg, I. *Acta Chem. Scand.* **16** (1962) 887.
2. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 747.
3. Schlyter, K. and Sillén, L. G. *Acta Chem. Scand.* **13** (1959) 385.
4. Schlyter, K. *Trans. Roy. Inst. Technol. Stockholm 1959*, No. 132.
5. Gerding, P., Leden, I. and Sunner, S. *Acta Chem. Scand.* **17** (1963) 2190.
6. Rossini, F. D. et al. *Selected Values of Chemical Thermodynamic Properties*, Natl. Bur. Std. Circ. 500, U. S. Government Printing Office, Washington 1952.
7. Hale, I. D., Izatt, R. M. and Christensen, I. I. *J. Phys. Chem.* **67** (1963) 2605.
8. Winkler, L. W. *Die chemische Analyse*, Stuttgart 1931, Vol. 29, p. 124ff.
9. Sillén, L. G. *Acta Chem. Scand.* **18** (1964) 1085.
10. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1964) 97.
11. Ingri, N., Lagerström, G., Frydman, M. and Sillén, L. G. *Acta Chem. Scand.* **11** (1957) 1034.
12. Arnek, R. *Arkiv Kemi* **24** (1965) 531.
13. Carell, B. and Olin, Å. *Acta Chem. Scand.* **16** (1962) 2350.
14. Carell, B. and Olin, Å. *Acta Chem. Scand.* **16** (1962) 2357.

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