780. *Values of log K, $\Delta H°$, and $\Delta S°$ at 25° for Stepwise Replacement of* Cl^- *by* OH^- *in Mercuric Chloride,* $HgCl_2(aq)$

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Reaction of OH^- with $HgCl_2(aq)$ in dilute solution has been found to give $HgClOH(aq)$ and $Hg(OH)_2(aq)$. Log K values at 25° and zero ionic strength for the stepwise formation of these complexes are 4·09 and 3·77, respectively. Corresponding $\Delta H°$ and $\Delta S°$ values are $-1·24$ kcal./mole and 14·6 e.u., and $-1·21$ kcal./mole and 13·2 e.u., respectively.

It was necessary to know the thermodynamic quantities associated with the hydrolysis of mercuric chloride [$HgCl_2(aq)$] as part of a study of the interaction of bidentate ligands with $HgCl_2(aq)$. The literature contained conflicting views about the species resulting from the hydrolysis of $HgCl_2(aq)$. Carrière and Lafitte[1] reported equilibrium constants for the formation of $HgCl_2OH^-$ and $HgCl_2(OH)_2{}^{2-}$, the latter being formed in more concentrated solutions. Carrière, Guiter, and Lafitte[2] stated that the hydrolysis can be represented by a series of reactions involving the formation of $HgClOH(aq)$, $(HgClOH)_2(aq)$, and $(HgCl_2OH)_2{}^{2-}$ at various concentrations of $HgCl_2$. Damm and Weiss[3] reported the product of hydrolysis to be $HgOH^+$ and gave an equilibrium constant for its formation. No heats for the hydrolysis of $HgCl_2(aq)$ have been reported.

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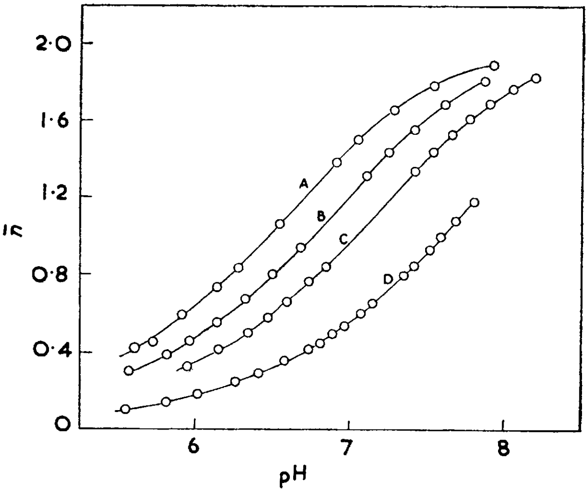
[1] E. Carrière and M. Lafitte, *Bull. Soc. chim. France*, 1945, **12**, 833.
[2] E. Carrière, H. Guiter, and M. Lafitte, *Bull. Soc. chim. France*, 1948, 23.
[3] K. Damm and A. Weiss, *Z. Naturforsch.*, 1955, **106**, 534.

In the present study, the species formed during the reaction of OH^- with $HgCl_2(aq)$ are established by computer analysis of pH titration results, and $\Delta G°$, $\Delta H°$, and $\Delta S°$ values are given for their formation at 25°.

EXPERIMENTAL

Materials.—Reagent grade mercuric chloride (Baker and Adamson), sodium hydroxide (" Baker Analysed "), and freshly boiled, double-distilled water of pH 6·3—6·8 were used in the preparation of solutions for the determinations.

Determination of Equilibrium Constants.—The equilibrium constants were obtained from pH titration results. Solutions of mercuric chloride having concentrations ranging from 0·004 to 0·00025F were titrated under a nitrogen atmosphere with a solution of sodium hydroxide, and pH measurements were made with a Leeds and Northrup pH meter (Cat. 7401) equipped with a 1000-ohm heliopot with a microdial setting, making the precision of the readings about ±0·004 pH unit. The Beckman glass and saturated calomel electrodes used in the determinations were calibrated against a buffer solution of pH 6·865, which was prepared from potassium dihydrogen phosphate and disodium hydrogen phosphate (National Bureau of Standards sample Nos. 186-I-b and 186-II-b, respectively) according to the instructions supplied by the National Bureau of Standards. Precipitation was observed in the 0·004F-solution of mercuric chloride when the $Na^+ : HgCl_2$ ratio exceeded 1·2. No precipitation was observed in the remaining solutions.



Plots of $\bar{n}$ against pH, with $[HgCl_2]_T$: A, 0·00025F; B, 0·0005F; C, 0·0010F; D, 0·0040F.

$$\bar{n} = \frac{\text{Total } OH^- \text{ bound to Hg(II)}}{[HgCl_2]_T}$$

$\Delta H°$ *Determinations.*—The heats of reaction were determined calorimetrically by titrating 0·00375F-mercuric chloride solutions with sodium hydroxide by a thermometric titration procedure.[4] The calorimeter in which the determinations were carried out has been described.[5] No precipitation was observed in these solutions before the end-point was reached ($2OH^-$ per $HgCl_2$). Precipitation was observed in a few solutions shortly after the end-point. The remaining solutions were apparently supersaturated with respect to some solid phase, possibly HgO [6] or an oxychloride of mercury(II). Only those runs in which no precipitation occurred were used in the calculation of $\Delta H°$.

Calculations.—The calculation of the correct equilibrium constants requires a knowledge of the reaction, or reactions, occurring during the pH titration. From the pH titration curve a distinct end-point was observed after the addition of 2 equivalents of OH^- per mole of mercuric chloride, indicating a maximum of $2OH^-$ per Hg(II). To test the system for possible formation of polynuclear species, the family of curves in the Figure was obtained. These curves, in which $\bar{n}$ is plotted against pH for a series of total mercuric chloride concentrations, $[HgCl_2]_T$, are

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[4] J. J. Christensen and R. M. Izatt, *J. Phys. Chem.*, 1962, **66**, 1030; R. M. Izatt, J. J. Christensen, R. Pack and R. Bench, *Inorg. Chem.*, 1962, **1**, 828.

[5] L. Hansen, J. J. Christensen, and R. M. Izatt, *Rev. Sci. Instr.*, 1965, **36**, in the press.

[6] A. B. Garrett and A. E. Hirschler, *J. Amer. Chem. Soc.*, 1938, **60**, 299.

similar to those obtained for a system in which polynuclear species exist; however, there is one important difference. In the Figure, as the total metal concentration increases at a given $\bar{n}$ value, the pH also increases. The reverse is true for the formation of polynuclear species.[7] The results in the Figure can be understood by considering a general reaction of the type

$$\mathrm{MA} + \mathrm{L} = \mathrm{ML} + \mathrm{A} \tag{1}$$

where M is a metal ion, and A and L are ligands. Then,

$$K = ([\mathrm{ML}]/[\mathrm{MA}])([\mathrm{A}]/[\mathrm{L}]) \tag{2}$$

and, with respect to ligand L,

$$\bar{n} = [\mathrm{ML}]/([\mathrm{MA}] + [\mathrm{ML}]) \tag{3}$$

Substituting (3) into (2) and solving for the product, K[L], one obtains

$$K[\mathrm{L}] = \bar{n}[\mathrm{A}]/(1 - \bar{n})$$

For two different titrations at different total metal concentrations,

$$K[\mathrm{L}] = \bar{n}[\mathrm{A}]/(1 - \bar{n}) \text{ and } K[\mathrm{L}]' = \bar{n}'[\mathrm{A}]'/(1 - \bar{n}')$$

If, now, $\bar{n} = \bar{n}'$, then $[\mathrm{L}]/[\mathrm{L}]' = [\mathrm{A}]/[\mathrm{A}]'$, and, since $[\mathrm{A}] = \bar{n}\mathrm{M_T}$, where $\mathrm{M_T}$ = total metal concn.,

$$[\mathrm{L}]/[\mathrm{L}]' = \mathrm{M_T}/\mathrm{M_T}'$$

Therefore, for a reaction of the general type defined by equation (1), [L] increases as the total metal concentration increases for a given $\bar{n}$ value. Thus, the results shown in the Figure provide evidence that the reaction(s) in this study are of the general type defined by equation (1), and that the overall reaction is

$$\mathrm{HgCl_2(aq) + 2OH^- = Hg(OH)_2(aq) + 2Cl^-}$$

The reactions were also investigated by using computer programmes based on the various reaction sequences given in equations (4)—(8).

$$\mathrm{HgCl_2(aq) + OH^- = HgClOH(aq) + Cl^-} \tag{4a}$$

$$\mathrm{HgClOH(aq) + OH^- = Hg(OH)_2(aq) + Cl^-} \tag{4b}$$

$$\mathrm{HgCl_2(aq) + OH^- = HgClOH(aq) + Cl^-} \tag{5a}$$

$$\mathrm{HgClOH(aq) + OH^- = HgCl(OH)_2^-} \tag{5b}$$

$$\mathrm{HgCl_2(aq) + OH^- = HgCl_2OH^-} \tag{6a}$$

$$\mathrm{HgCl_2OH^- + OH^- = HgCl_2(OH)_2^{2-}} \tag{6b}$$

$$\mathrm{HgCl_2(aq) + OH^- = HgCl_2OH^-} \tag{7a}$$

$$\mathrm{HgCl_2(aq) + HgCl_2OH^- = (HgCl_2)_2OH^-} \tag{7b}$$

$$\mathrm{HgCl_2OH^- + OH^- = HgCl_2(OH)_2^{2-}} \tag{7c}$$

$$\mathrm{HgCl_2(aq) + 2OH^- = HgCl_2(OH)_2^{2-}} \tag{8}$$

Apparent thermodynamic equilibrium constants for each set of proposed reactions (4—8) were calculated from the pH titration results by using equation (9), as has been described previously.[8] The several terms in equation (9) have their usual significance.[9] Equation (9) in which

$$\log \gamma = -AZ^2\sqrt{\mu}/(1 + B\mathring{a}\sqrt{\mu}) \tag{9}$$

$\mathring{a}$ had a value of 4 Å was used to convert pH and K_W (ionic product of water) into the corresponding

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[7] F. J. C. Rossotti and H. Rossotti, " The Determination of Stability Constants," McGraw-Hill, New York, 1961, p. 355.

[8] R. M. Izatt, C. G. Haas, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, 1954, **58**, 1133.

[9] H. S. Harned and B. B. Owen, " The Physical Chemistry of Electrolytic Solutions," 3rd edn., Reinhold, New York, 1958, ch. 5.

concentration quantities at each experimental point, and to correct concentration constants to thermodynamic constants.

Constant log K values as a function of $\bar{n}$ and $[HgCl_2]_T$ were obtained only for the reaction sequence represented by equations (4a and b), confirming the evidence presented in the Figure for replacement of Cl^- by OH^-.

Heats of reaction for equations (4a and b) were calculated from the thermometric titration results as described previously.[10]

The calculations were aided by an IBM 7040 computer.

RESULTS AND DISCUSSION

Log K_1 and log K_2 values for equations (4a and b), respectively, are given in Table 1. A typical set of log K values, calculated on the assumption that equations (6a and b) represent the correct reaction sequence, is given in Table 2.

The log K_1 values in Table 2 vary significantly both with changing $[HgCl_2]_T$ values and with $\bar{n}$ at a given $[HgCl_2]_T$ value, whilst the log K_2 values show little variation with changing $\bar{n}$ at a given $[HgCl_2]_T$ value, but vary significantly with changing $[HgCl_2]_T$ values. Thus, the figures in Table 2 show that equations (6a and b) do not describe the reactions occurring in the system. Figures similar to those in Table 2 were obtained for the reaction sequences suggested in equations (5), (7), and (8).

TABLE 1

Log K_1 and log K_2 values at 25° and zero ionic strength for reactions (4a) (log K_1) and (4b) (log K_2)

(Uncertainties are given as standard deviations. $[HgCl_2]_T$ refers to the formal $HgCl_2$ concentration)

$[HgCl_2]_T$	0·004	0·001	0·0005	0.00025
Log K_1	4·09 ± 0·02	4·09 ± 0·01	4·07 ± 0·02	4·06 ± 0·02
Log K_2	3·77 ± 0·02	3·77 ± 0·01	3·77 ± 0·01	3·75 ± 0·02

TABLE 2

Log K_1 and log K_2 values calculated by assuming that equations (6a and b) represent the correct reactions in the $HgCl_2(aq)$–OH^- system

$\bar{n}$	0·001F-$HgCl_2$ Log K_1	0·0005F-$HgCl_2$ Log K_1	0·00025F-$HgCl_2$ Log K_1	$\bar{n}$	0·001F-$HgCl_2$ Log K_2	0·0005F-$HgCl_2$ Log K_2	0·00025F-$HgCl_2$ Log K_2
0·30	7·71	7·96	8·23	1·30	6·36	6·67	—
0·40	7·64	7·91	8·18	1·40	6·36	6·68	6·98
0·50	7·57	7·86	8·14	1·50	6·38	6·69	7·00
0·60	7·53	7·82	8·11	1·60	6·38	6·70	7·00
0·70	7·50	7·78	8·06	1·70	6·40	6·71	7·00

Values of ΔH°_1 and ΔH°_2 for equations (4a and b), respectively, calculated from the thermomometric titration results together with corresponding ΔG° and ΔS° values are given in Table 3.

TABLE 3

Thermodynamic quantities for equations (4a and b) at 25°

(Uncertainty of the ΔH°_i values is the standard deviation based on four runs while that of the ΔG°_i values is estimated from the corresponding uncertainties of the log K_i values in Table 1.)

Reaction	ΔG°_i (kcal./mole)	ΔH°_i (kcal./mole)	ΔS°_i (e.u.)	$T\Delta S^\circ_i$ (kcal./mole)
Eqn. (4a)	−5·58 ± 0·02	−1·24 ± 0·03	+14·6 ± 0·1	4·34 ± 0·03
,, (4b)	−5·14 ± 0·02	−1·21 ± 0·06	+13·2 ± 0·1	3·93 ± 0·04

In this study the species formed by the hydrolysis of $HgCl_2(aq)$ are established. Since the reaction sequence differs from those reported previously, no comparison of equilibrium constants is made.

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[10] J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. D. Hale, *Inorg. Chem.*, 1964, **3**, 130; L. D. Hansen, Ph.D. Dissertation, Brigham Young University, Provo, Utah, 1965.

The figures in Table 2 show the necessity of making determinations of equilibrium constants both as a function of total metal concentration and $\bar{n}$, since consistent log K_i values under a single set of experimental conditions do not constitute reliable evidence for a suggested reaction.

The values in Table 3 show that the small differences between ΔH°_1 and ΔH°_2, and between ΔS°_1 and ΔS°_2 cause the log K_1 and log K_2 values to be nearly equal. It is apparent from these figures that the main contribution to ΔG°_i is made by the $T\Delta S^{\circ}_i$ term. From the entropies of the hydrated ions[11] ($S^{\circ}_{\text{OH}^-} = -2{\cdot}52$ e.u., $S^{\circ}_{\text{Cl}^-} = +13{\cdot}2$ e.u.) it is evident that almost the entire entropy change accompanying reactions (4a and b) is due to the difference in the absolute entropies of the aqueous OH^- and Cl^- ions, and that the entropies of the neutral species, $HgCl_2$(aq), HgClOH(aq), and $Hg(OH)_2$(aq) are all approximately equal. It is, therefore, seen that the primary driving force in reactions (4a and b) is the entropy increase in the system resulting from the difference in entropies of the OH^- and Cl^- ions. The ΔG°_2 value in Table 3 is slightly less negative than the ΔG°_1 value which is seen to be a result of $T\Delta S^{\circ}_2$ being smaller than $T\Delta S^{\circ}_1$; ΔH°_2 and ΔH°_1 being equal within experimental uncertainty.

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[11] W. M. Latimer, " Oxidation Potentials," 2nd edn., Prentice-Hall, New York, 1952, pp. 39, 54.