$K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$, dissolves to form a red solution, the impressive wine-red color observed during the *reduction* of chlorotungstates[28] is still unexplained. Therefore we have measured the absorption spectra of samples taken after different reduction times from chlorotungstate solutions reduced with tin below the oxidation state +4. All the spectra of red solutions obtained in this way showed two bands at 19,100 and ~22,730 cm.$^{-1}$, respectively, with different intensity ratios depending on external conditions. They usually fit into the sequence of spectra obtained in Fig. 2.

Therefore, even if the results available at present are not sufficient to disprove the existence of a red tungsten(III) definitely, it seems probable that the existence of red tungsten(III) is simulated during the reduction of chlorotungstates in a like manner as in the case of the disproportionation of $K_2[W(OH)Cl_5]$. The red solutions simply contain the two ions $[W_2Cl_9]^{3-}$ and $[W(OH)Cl_5]^{2-}$. If this is assumed to be the case, all the former observations of red tungsten solutions[28] obtained as the product of reduction of tungsten(VI) may easily be understood because of the very high intensity of the 19,100 cm.$^{-1}$ band in the absorption spectrum of $K_2[W(OH)Cl_5]$.[29]

Apparently the formation of $K_2[W(OH)Cl_5]$ from tungsten(V) and from tungsten(III) complex ions during the reduction of chlorotungstates in strong HCl, as well as its disproportionation into these ions, follow reaction schemes that may be closely related. Which one of these reactions is preferred seems to depend on the concentration of the tungsten species involved as well as on the concentration of $Cl^-$ ions only.

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[28] (a) Olsson[5] observed that during the reduction of chlorotungstates in strong HCl with tin a transient red solution is formed. (b) Using a lead cathode Collenberg and Backer[4a] obtained red solutions with a tinge of yellow and an oxidation number of +3.02 by reduction of potassium chlorotungstate solutions in concentrated HCl at 18°. Higher temperatures (35 to 50°) produced directly the yellow-green $[W_2Cl_9]^{3-}$ ion. Sometimes the reduction of sodium chlorotungstate solutions produced clear red solutions with oxidation numbers >3.06. From these solutions RbCl precipitated a dark red substance, an empirical formula $Rb_2[W(H_2O)Cl_5]$ having been proposed, but the authors confess that the composition of different preparations fluctuated widely. (c) Lingane and Small[2] obtained red tungsten solutions during the coulometric reduction of tungsten(V) in 12 *M* HCl at 18°, the oxidation state having been found to be +3.09. The existence of a red tunsten(III) has been postulated and an absorption spectrum exhibiting one single band at 19,050 cm.$^{-1}$ ($\epsilon$ ~560) was reported. They avoided carrying out the reduction to completion, because then the yellow-green $[W_2Cl_9]^{3-}$ ion is obtained. (d) Laudise and Young[7] reported the preparation of $K_5[W_3Cl_{14}]$, the $[W_3Cl_{14}]^{5-}$ ion having been reported as giving a deep red solution with an absorption band at 19,400 cm.$^{-1}$. They found an oxidation state of +3.22; as to the nature of this substance see above. (e) Hawkins and Garner[26] observed that during the decomposition of the $[W_2Cl_9]^{3-}$ ion the solutions often turn red and at the same time a broadening of the base of the 22,200 cm.$^{-1}$ peak has been observed.

[29] In consequence of the high intensity of the 19,100 cm.$^{-1}$ peak ($\epsilon$ ~10,000) of $K_2[W(OH)Cl_5]$, solutions containing almost the total tungsten as tungsten(III) and only a small part as $K_2[W(OH)Cl_5]$ may still be red or even show a tinge of red. Therefore usually an oxidation state slightly higher than +3.00 has been found for the so-called "red tungsten(III)" solutions.[28b,c,d]

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING,
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# Thermodynamics of Metal–Halide Coordination in Aqueous Solution. I. Equilibrium Constants for Several Mercury(I)- and Mercury(II)–Halide Systems as a Function of Temperature[1a]

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Equilibrium constants have been determined for the stepwise formation at 7 and 40° of $HgX_2(aq)$ (X = Cl, Br, I) from $Hg^{+2}$ and $X^-$ (also at 25° in the case of $Cl^-$). Solubility product constants for $Hg_2X_2$ at 7 and 40° and the solubility of $HgI_2$ at 8, 25, and 40° have also been determined. All data are valid in a solvent 0.10 *F* in $HClO_4$ and 0.40 *F* in $NaClO_4$.

## Introduction

Important theoretical advances[2,3] in recent years have resulted in a better understanding of the nature of the bonding forces in coordination compounds. However, the quantitative thermodynamic data needed to evaluate these theories in the case of complex ions in aqueous solution are, in many cases, not known. Particularly scarce are calorimetrically determined $\Delta H°$ and corresponding $\Delta S°$ values for metal–ligand interaction.

Extensive studies[4,5] of the stabilities of halide complexes of the elements in aqueous solution indicate that

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[1] (a) Supported by the Atomic Energy Commission, Contract No. AT(04-3)-299. Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963. (b) To whom correspondence concerning this article should be addressed.

[2] P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).

[3] L. F. Orgel, "An Introduction to Transition-Metal Chemistry, Ligand Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960.

[4] S. Ahrland, *et al., Quart. Rev.* (London), **12**, 265 (1958).

[5] S. Ahrland, *Acta Chem. Scand.*, **10**, 723 (1956).

acceptor atoms can be classified into two groups according to whether the formation constant of the complex species decreases in the order (A) $F^- >> Cl^- > Br^- > I^-$ or (B) $I^- > Br^- > Cl^- >> F^-$.

The stabilities of the halo complexes formed by most acceptor atoms show them to possess type A character; however, a small number of metal ions at, or near, the end of each transition series show type B behavior.[5] No completely satisfactory explanation has been given to explain the existence of these two types of acceptor atoms.

This paper is the first of a series designed to provide quantitative, thermodynamic data as a function of temperature for the interaction in aqueous solution of $X^-$ (X = Cl, Br, I) with type B metal ions. It is hoped that these data will provide greater insight into the nature of the metal-halide bonds in the resulting species. $Cl^-$, $Br^-$, and $I^-$ have been selected as the ligands since they comprise a series of simple, closely related anions which interact strongly with many type B metal ions, thus providing for study a series of closely related complexes of high stability.

Mercuric ion was chosen for initial study because (a) it exists as the hydrated ion in acidic solutions, less than 0.1% being hydrolyzed below pH 1,[6] (b) it is a typical type B metal ion, (c) its interaction with $X^-$ at 25° has been studied previously, providing a check on equilibrium constants determined here, and (d) precipitation does not occur upon addition of $X^-$, except in the case of $HgI_2$. The formation of $HgI_2(s)$ in the solutions under study necessitated the determination of its solubility as a function of temperature in order to be able to calculate from the experimental data equilibrium constants for the formation of $HgI_2(aq)$.

Equilibrium constants for the stepwise interaction of $X^-$ with $Hg^{+2}$ are difficult to obtain because no direct and few indirect procedures are available for measuring the free $[X^-]$ in equilibrium with the mercury-containing species. Several methods have been used to study $Hg^{+2}$–$X^-$ equilibria in aqueous solution and numerous equilibrium constant determinations have been reported at temperatures near 25°.[7] In a series of papers dealing with mercuric ion–halide ion interaction at 25°, Sillén[8] has reviewed earlier work, enumerated the difficulties encountered by previous investigators, and developed a potentiometric method for determination of the equilibrium constants for the stepwise interaction of $X^-$ with $Hg^{+2}$. No thermodynamic studies as a function of temperature have been reported for the formation of $HgX_2$ from $Hg^{+2}$ and $X^-$ in aqueous solution.

Biedermann and Sillén[9] have determined the solubility of $HgI_2$ in 0.50 $F$ $NaClO_4$ at 25° and have reviewed earlier work on the solubility of this compound in aqueous solutions. Van Eck[10] has determined extinctometrically the change with temperature of $HgI_2$ solubility in a solvent 0.5 $F$ in $NaClO_4$ and 0.01 $F$ in $HClO_4$; however, he does not give specific values for the solubility at any of the temperatures studied, 25, 35, and 40°.

Formation constants are reported in the present study for the stepwise interaction of $X^-$ with $Hg^{+2}$ to form $HgX_2$ at 7 and 40° (also at 25° in the case of $Cl^-$). Solubility product constants for $Hg_2X_2$ at 7 and 40° and the solubility of $HgI_2$ at 8, 25, and 40° are also given. All reported data are valid in a solvent which is 0.10 $F$ in $HClO_4$ and 0.40 $F$ in $NaClO_4$ (ionic strength $\mu$ = 0.50). The $HClO_4$ was necessary to minimize $Hg^{+2}$ hydrolysis, and the $NaClO_4$ was added to maintain a $\mu$ value sufficiently high that $\mu$ would not change appreciably during the titrations.

## Experimental

**Materials.**—Solutions of $HClO_4$, $NaClO_4$, NaCl, NaBr, and NaI were prepared from reagents of highest available purity and were standardized by conventional means. The $HgI_2$ used for the solubility studies was Fisher Certified Reagent Grade. A mercuric perchlorate stock solution was prepared by dissolving a weighed amount of reagent grade (100.0%) HgO in a known volume of standard $HClO_4$. The $[Hg^{+2}]$ was checked by titration with KSCN. Mercurous solutions were prepared by equilibrating an excess of Hg(l) and concentrated $HClO_4$ with HgO and then filtering off the excess Hg(l). The solution thus obtained was standardized by oxidizing the $Hg_2^{+2}$ with $KMnO_4$ and titrating the resulting $Hg^{+2}$ with KSCN. The quantity of $Hg^{+2}$ in the $Hg_2^{+2}$ solution was obtained from e.m.f. measurements as described by Sillén.[8]

**Procedure for Equilibrium Constant Determination.**—The method was identical with that used by Sillén[8] except that (a) $E^0$ for $2Hg(l) = Hg_2^{+2}(aq) + 2e^-$ was determined by measuring the potentials of dilutions of $Hg_2^{+2}$ solutions rather than from the first part of the titration curve of $Hg_2^{+2}$ with $X^-$, (b) $E^0$ for the reaction $2Hg(l) + 2X^- = Hg_2X_2(s) + 2e^-$ was measured by titration of a saturated solution of freshly prepared $Hg_2X_2$ with $X^-$ rather than from the second part of the titration of $Hg_2^{+2}$ with $X^-$, (c) the $HClO_4$ concentration was 0.10 $F$ in the present study (0.010 $F$ in that of Sillén) although total ionic strength was the same in the two studies (0.50 $F$), and (d) the present study was carried out at 7 and 40° with only the $Hg^{+2}$–$Cl^-$ system being studied at 25° in order to check the agreement between the present results and those of Sillén.

**Measurement of $HgI_2$ Solubility.**—Solid $HgI_2$ was equilibrated with 0.40 $F$ $NaClO_4$–0.10 $F$ $HClO_4$ solutions at 8, 25, and 40°. This was done by placing the solid $HgI_2$ in 500 ml. plastic bottles which were filled approximately $^3/_4$ full with solvent, and attaching the bottles to a rotating drum within a large (4 × 2 × 2 ft.) water bath maintained at the desired temperature. The supernatant solution was analyzed after 1 week for total mercury by precipitation of the dissolved mercury as HgS and weighing as HgS on a microbalance after careful drying at 110°. It was assumed that equilibrium was obtained within 1 week since solutions left in the water bath for 3 weeks gave the same results within experimental error.

**Equilibrium Constant Calculations.**—Equilibrium constants were calculated from our data using the same method as described by Sillén.[8]

## Results

In Table I are given the formation constants for the stepwise interaction of $X^-$ with $Hg^{+2}$ at 7 and 40° (also at 25° in the case of $Cl^-$) together with the solu-

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(6) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.* **6**, 747 (1952).

(7) "Stability Constants; Part II: Inorganic Ligands," compiled by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, Special Publication 7, The Chemical Society, London, 1958.

(8) See L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949), and earlier papers cited therein.

(9) G. Biedermann and L. G. Sillén, *Svensk. Kem. Tidskr.*, **61**, 63 (1949).

(10) C. L. Van Panthaleon Van Eck, Ph.D. Thesis, University of Leiden, 1958.

TABLE I

EQUILIBRIUM CONSTANTS FOR SEVERAL MERCURY–HALIDE EQUILIBRIA IN AQUEOUS SOLUTION

| Reaction | $T$, °C. | $Cl^-$ | $Br^-$ | $I^-$ |
|---|---|---|---|---|
| | | | Formation constant, $K_n$ | |
| (1) $Hg^{+2} + X^- = HgX^+$ | 7 | $17 \times 10^6$ | $3.4 \times 10^9$ | $38 \times 10^{12}$ |
| | 25 | $4.2 \times 10^6$<br>$(5.5 \times 10^6)^a$ | $(1.1 \times 10^9)^a$ | $(7.3 \times 10^{12})^a$ |
| | 40 | $3.8 \times 10^6$ | $0.50 \times 10^9$ | $2.5 \times 10^{12}$ |
| (2) $HgX^+ + X^- = HgX_2(aq)$ | 7 | $5.3 \times 10^6$ | $7.0 \times 10^8$ | $43 \times 10^{10}$ |
| | 25 | $2.3 \times 10^6$<br>$(3.0 \times 10^6)^a$ | $(2.0 \times 10^8)^a$ | $(8.9 \times 10^{10})^a$ |
| | 40 | $1.5 \times 10^6$ | $0.57 \times 10^8$ | $3.4 \times 10^{10}$ |
| (3) $HgX^+ + X^- = HgX_2(s)$ | 7 | | | $16 \times 10^{15}$ |
| | 25 | | | $(1.2 \times 10^{15})^a$ |
| | 40 | | | $0.26 \times 10^{15}$ |
| | | | Solubility product constant, $K_{sp}$ | |
| (4) $Hg_2X_2(s) = Hg_2^{+2} + 2X^-$ | 7 | $6.5 \times 10^{-19}$ | $1.4 \times 10^{-23}$ | $4.6 \times 10^{-30}$ |
| | 25 | $(1.3 \times 10^{-17})^a$ | $(5.2 \times 10^{-22})^a$ | $(3.4 \times 10^{-28})^a$ |
| | 40 | $6.9 \times 10^{-17}$ | $6.7 \times 10^{-21}$ | $3.5 \times 10^{-27}$ |

[a] Reference 8.

bility product constants for the three mercury(I) halides at 7 and 40°. The estimated uncertainty in the equilibrium constants ($C \times 10^n$) is $C \pm 0.5$ for reactions 1, 2, and 3 and $C \pm 0.1$ for reaction 4. Included in Table I are values taken from Sillén.[8]

**$HgI_2$ Solubility.**—The formal solubility of $HgI_2(s)$ was determined at 8, 25, and 40° to be $(3.7 \pm 0.4) \times 10^{-5}$, $(8.2 \pm 0.4) \times 10^{-5}$, and $(13.4 \pm 0.2) \times 10^{-5}$, respectively. These values are for the reaction $HgI_2(s) = HgI_2(aq)$ and are valid in a solvent 0.40 $F$ in $NaClO_4$ and 0.10 $F$ in $HClO_4$. Biedermann and Sillén[9] found $(7.4 \pm 0.3) \times 10^{-5}$ at 25° in a slightly different solvent (0.010 $F$ $HClO_4$ rather than 0.1 $F$ $HClO_4$ at $\mu = 0.5$).

## Discussion

The $Hg^{+2}$–$Cl^-$ data in Table I for reactions 1 and 2 at 25° are seen to be in good agreement with those of Sillén.

The $K_n$ data in Table I show the successive constants in the formation of $HgX_2(aq)$ to decrease from 7 to 40°. At a given temperature $K_2 < K_1$ in all cases. The greatest difference between $K_1$ and $K_2$ is found in the case of $I^-$ at each temperature, and this difference increases from 7 to 40°.

$K_{sp}$ values at a given temperature increase in the order I < Br < Cl.

In Table II are given the $\Delta G°$ values calculated from the data in Table I for the several $Hg^{+2}$–$X^-$ systems. The precision of the values is ±0.2 kcal. mole.

TABLE II

$-\Delta G°$ VALUES (KCAL./MOLE) AS A FUNCTION OF TEMPERATURE FOR STEPWISE INTERACTION OF $X^-$ WITH $Hg^{+2}$. VALUES FOR 25° CALCULATED FROM DATA IN REF. 8.

| | | | $-\Delta G°$ | |
|---|---|---|---|---|
| Reaction | $T$, °C. | $Cl^-$ | $Br^-$ | $I^-$ |
| (1) $Hg^{+2} + X^- = HgX^+$ | 7 | 9.3 | 12.2 | 17.4 |
| | 25 | 9.2 | 12.3 | 17.5 |
| | 40 | 9.4 | 12.5 | 17.8 |
| (2) $HgX^+ + X^- = HgX_2(aq)$ | 7 | 8.6 | 11.3 | 14.9 |
| | 25 | 8.8 | 11.3 | 15.0 |
| | 40 | 8.8 | 11.1 | 15.1 |
| (3) $HgX^+ + X^- = HgX_2(s)$ | 7 | | | 20.8 |
| | 25 | | | 20.6 |
| | 40 | | | 20.3 |

The data in Table II show that the $\Delta G°$ values do not change significantly with temperature, indicating the temperature and $K_n$ changes just compensate each other. Further discussion of $\Delta G°$ values will appear in part II,[11] where calorimetric $\Delta H°$ and corresponding $\Delta S°$ values as a function of temperature will be reported.

**Acknowledgment.**—The authors wish to express thanks to Dr. John D. Hale for many helpful discussions.

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(11) J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. D. Hale, *Inorg. Chem.*, in press.