tively large cavities of the WO_3 structure. On cooling, the WO_3 lattice need not revert to its original monoclinic structure because there would now be an increased entropy contribution from the mixing of empty cavities and cavities occupied by silver atoms. If the enthalpy change between the monoclinic and rhombic varieties of WO_3 is small (and it is probably no more than a hundred calories or so) and if the doping with Ag produces no significant decrease in the vibrational entropy contribution for the WO_3 structure, then the configurational entropy, though only of the order of 0.09 e.u., may be sufficient to stabilize the orthorhombic crystal structure at room temperature.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

A Calorimetric Determination of the Values of ΔH^0 for Mercury(II)–Halide Complex Ion Reactions and the Derived Values of ΔS^0[1,2a,b]

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The values of ΔH^0 for the reactions $HgCl_{n-1}^{+3-n} + Cl^- = HgCl_n^{+2-n}$ (n = 1 to 4) and $Hg^{+2} + 4X^- = HgX_4^{=}$ (X^- = Br^- and I^-) in solutions of ionic strength = 0.5 M determined by calorimetric measurements are −5.9, −6.9, −2.2, +0.1 −27.7 and −44.3 kcal., respectively. Coupled with the equilibrium quotient values obtained by Sillen and co-workers, and by Marcus, this study permits the evaluation of the entropy changes accompanying these reactions. The abnormally positive value of the entropy change in the fourth stepwise mercury(II)–chloride reaction suggests that a decrease in coordination number of mercury(II) occurs in this reaction. With some of the data obtained here in combination with data on mercury(II)–bromide reactions reported by Scaife and Tyrrell, one can demonstrate the validity of the Latimer and Jolly method of calculating the "replacement" contribution to value of ΔS^0.

Although it is often assumed that the coördination number of a metal ion remains constant in its complex ion formation reactions, there are certainly some systems in which this is not the case. That the mercury(II)–chloride complex ion system, with the reactions

$$HgCl_{n-1}^{+3-n} + Cl^- = HgCl_n^{+2-n}$$

where n = 1 to 4, may be an example was suggested by van Panthaleon van Eck on the basis of X-ray diffraction of aqueous solutions containing mercury(II) ion and chloride ion.[3] These data[3] were interpreted in terms of a coördination number of six for mercury(II) in the species with zero,[4] one and two chloride ions, and a coördination number of four for mercury(II) in the species with four chloride ions; a coördination number of five was suggested by van Panthaleon van Eck for the species with three chloride ions, although this was admitted to be uncertain.[3b] There are theoretical arguments for a distorted ~~octahedral~~ configuration of ligands about mercury(II).[5]

The present paper deals primarily with calorimetric experiments which establish the values of ΔH^0 for the mercury(II)–chloride complex ion formation reactions in aqueous solution at 25°. The ionic strength of the final solutions was 0.5 M, with the principal cationic contributor being hydrogen ion. In all solutions except those in which the tetrahalide species formed to a significant extent, the principal anionic species present was perchlorate ion. In the interpretation of these calorimetric studies, it was assumed that the value of each relevant quotient of activity coefficients was constant and had the same value as is appropriate for solutions of ionic strength equal to 0.5 M in which the principal cationic species was sodium ion; this was the medium in which Sillen[6a] and Marcus[6b] established the values of the equilibrium quotients. The mercury(II) concentration in the present work was less than 0.05 M; it is assumed that further dilution of the mercury(II) species would result in no heat effect. The standard state for the solute species in this study is a hypothetical one molar solution in which the ionic strength is 0.5 M. The zero superscript when used with ΔF, ΔH and ΔS pertain to the standard changes in these quantities referred to this standard state.

The ΔS^0 values can be derived from the combination of the ΔH^0 values obtained in this work and the ΔF^0 values established by Sillen[6a] and Marcus.[6b] It is anticipated that any reaction in which a change in the coördination number occurs will have associated with it a standard entropy change which is abnormal compared to the values associated with reactions in which there is no such change. The big problem is deciding what a normal ΔS^0 value would be. The standard entropy changes for a series of complex ion formation reactions without coördination number change, after appropriate correction for the symmetry number factor, may, perhaps, be expected to conform to the equation[7]

$$\Delta S^0_{\text{cor}} = a - b\Delta Z^2 \qquad (1)$$

where ΔZ^2 is the sum of the squares of the charges

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[1] This work was supported in part by grants from the United States Atomic Energy Commission (Contract No. AT(11-1)-64, Project No. 3), and the Research Committee of the Graduate School, University of Wisconsin.

[2] (a) Presented in part at the 135th National meeting of the American Chemical Society, Boston, Massachusetts, April, 1959. (b) Taken in part from the Ph.D. thesis of Patrick K. Gallagher, University of Wisconsin, 1959.

[3] (a) C. L. van Panthaleon van Eck, H. B. M. Wolters and W. J. M. Jaspers, *Rec. trav. chim.*, **75**, 802 (1956); (b) C. L. van Panthaleon van Eck, Thesis, Leiden (1958).

[4] (a) In hexagonal mercury(II) oxide, each mercury(II) is surrounded by a distorted octahedron of oxygen atoms; K. Aurivillius and I. B. Carlsson, *Acta Chem. Scand.*, **12**, 1297 (1958). (b) Aquozinc (II) ion in aqueous solution has been shown to be $Zn(OH_2)_6^{+2}$; F. A. Cotton and H. P. Hansen, *J. Chem. Phys.*, **28**, 83 (1958).

[5] L. E. Orgel, *J. Chem. Soc.*, 4186 (1958).

[6] (a) L. G. Sillen, *Acta Chem. Scand.*, **3**, 539 (1949); (b) Y. Marcus, *ibid.*, **11**, 599 (1957).

[7] (a) E. L. King, *J. Phys. Chem.*, **63**, 1070 (1959); (b) E. L. King and P. K. Gallagher, *ibid.*, **63**, 1073 (1959).

on the products minus the sum of the squares of the charges on the reactants. The basis of this expectation is the successful correlation of the values of $\Delta S^0_{\mathrm{cor}}$ with equation 1 for the first five successive aluminum(III)–fluoride complex ion formation reactions and the first three successive scandium(III)–fluoride complex ion formation reactions.[8] It must be admitted, however, that equation 1 has not yet been shown to correlate the values of the entropy change in a series of normal chloride complexing reactions; there does not appear to be any well-studied system with the requisite number of steps.

Calorimetric studies also have been made of the over-all reaction

$$Hg^{++} + 4X^- = HgX_4^= \qquad (4')$$

for $X^- = Br^-$ and I^-. The ΔS^0 values derived from these data and some values for other mercury(II)–bromide reactions reported by Scaife and Tyrrell[9] allow tests of the Latimer and Jolly method[10] of considering the ΔS^0 values for complex ion formation reactions to include a "replacement" effect of predictable magnitude in addition to a "charge" effect.

Experimental

The Calorimeter.—The calorimeter was, with some modifications, that constructed by Dr. K. Schug; this equipment and its use already have been described.[11] The calorimeter was calibrated periodically during the course of this work. Fourteen determinations of the heat evolved upon dissolving magnesium metal in 1.000 *M* hydrochloric acid gave values in the range 109.6 to 112.7 kcal./g. atom of magnesium; an accurately determined value of this quantity is 111.32 kcal.[12] Fourteen determinations of the heat absorbed upon dissolving crystalline potassium chloride in water to give solutions with a concentration in the range 0.07 to 0.14 molal gave values between 4.15 and 4.22 kcal./mole of potassium chloride; the average of the observed values was 4.20 kcal./mole. The literature values of this quantity for these concentration extremes are 4.193 and 4.202 kcal./mole.[13]

Reagents.—All solutions used in this work were prepared with doubly distilled water using reagent grade chemicals unless otherwise specified. The second distillation of the water was from an alkaline permanganate solution in a Barnstead still.

The mercury(II) perchlorate stock solution was prepared by dissolving mercury(II) oxide in excess perchloric acid. The concentration of excess acid was determined by passing portions of the solution through a column of Dowex 50 resin in the hydrogen ion form. The effluent and washings were titrated with base of known concentration.

In some experiments, a perchlorate of lithium, sodium, magnesium or barium was used in place of perchloric acid to maintain constant ionic strength. Stock solutions of each of these substances were prepared from the appropriate G. F. Smith reagent which had been twice recrystallized from water. The solutions were standardized by passing portions through a column of Dowex 50 resin in the hydrogen ion form and titrating the effluent acid and washings with standard base.

Experiments in which Mercury(II)–Perchlorate Solution was Added to Hydrochloric Acid–Perchloric Acid Solution.—In nineteen experiments, samples of 2.00 to 5.00 ml. of mercury(II)–perchlorate solution (1.849 *M* $Hg(ClO_4)_2$, 0.526 *M* $HClO_4$) were added to 300 ml. of perchloric acid–hydrochloric acid of such a composition that the final value of the ionic strength was 0.50 ± 0.05 *M*. The concentration of free chloride ion in the final solution was calculated from the stoichiometric composition and the appropriate equilibrium quotient values.[6] The observed evolved heat was corrected for the heat of dilution of the mercury(II) perchlorate solution into a perchloric acid solution of ionic strength 0.50 *M*, which was found to be −0.9 ± 0.1 kcal./mole. The 10% uncertainty in the value of the heat of dilution contributes, in most of the experiments, an uncertainty of 1% or less to the quantity of heat being attributed to the chemical reactions. The results of these experiments are summarized in Table I.

TABLE I

THE HEAT EVOLVED UPON ADDING MERCURY(II) PERCHLORATE SOLUTION TO HYDROCHLORIC ACID–PERCHLORIC ACID SOLUTION

$T = 25.0 \pm 0.2°$ $I = 0.50 \pm 0.05\ M$

	Mercury(II) (mmole)	$[Cl^-]$[a]	Heat evolved (kcal./mole Hg^{II})		
			$\bar{n}$[a]	Obsd.[b]	Calcd.[c]
1[d]	9.25	9.77×10^{-8}	0.50	3.06	3.06
2[d]	7.40	9.77×10^{-8}	0.50	3.07	3.06
3	9.25	2.40×10^{-7}	0.985	6.13	6.13
4[d]	9.25	2.46×10^{-7}	1.00	6.22	6.20
5[d]	7.40	2.46×10^{-7}	1.00	6.23	6.20
6	7.40	2.50×10^{-7}	1.01	6.37	6.28
7[d]	9.25	6.16×10^{-7}	1.50	9.42	9.41
8[d]	7.40	6.16×10^{-7}	1.50	9.38	9.41
9	7.40	1.0×10^{-4}	2.00	12.83	12.8
10	9.25	1.0×10^{-4}	2.00	12.85	12.8
11	5.55	1.0×10^{-4}	2.00	12.96	12.8
12	3.70	1.0×10^{-4}	2.00	12.73	12.8
13	9.25	1.0×10^{-4}	2.00	12.89	12.8
14	7.40	8.0×10^{-2}	2.84	14.00	14.0
15	9.25	2.7×10^{-1}	3.59	15.01	14.7
16	5.55	3.2×10^{-1}	3.66	14.36	14.8
17	7.40	3.4×10^{-1}	3.68	14.82	14.8
18	9.25	4.0×10^{-1}	3.72	14.74	14.8
19	3.70	4.0×10^{-1}	3.72	14.72	14.8

[a] The values of the molarity of uncombined chloride ion, $[Cl^-]$, and the average number of chloride ions bound per mercury(II) ion, $\bar{n}$, were calculated from the stoichiometric composition and the appropriate equilibrium quotient values.[6] [b] Corrected for the heat of dilution of the mercury(II) perchlorate solution. [c] Calculated using the ΔH_n values given in Table V. [d] In these experiments, the final volume in the calorimeter was 350–360 ml.

Experiments in which $[\Delta H_1 + \Delta H_2]$ was Evaluated in Solutions Containing Different Electrolytes.—Dichloromercury(II) is particularly stable with respect to species containing one more and one less chloride ion ($[HgCl_2] = 4.1 \times 10^6 \times \sqrt{[HgCl^+][HgCl_3^-]}$ at 25° and $I = 0.5\ M$[6]); upon bringing mercury(II) ion and chloride ion together in the proportions two chloride ions per mercury(II) ion, the reaction

$$Hg^{++} + 2Cl^- = HgCl_2 \qquad (2')$$

occurs essentially to completion. This reaction is, therefore, a convenient one to study for a possible medium effect upon the enthalpy change. Experiments of the same type as described in the preceding section were performed in which the hydrogen ion concentration was 0.1 *M* and in which the perchlorates of lithium, sodium, magnesium and barium were used to maintain the ionic strength at 0.5 *M*. With each of these cations as the principal cationic contributor to the ionic strength, three experiments were performed to determine the heat of dilution of the mercury(II) perchlorate stock solution, and three experiments were performed with chloride ion present. The average values of the heat of dilution to give a solution with a concentration of

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[8] J. W. Kury, A. D. Paul, L. G. Hepler and R. E. Connick, THIS JOURNAL, **81**, 4185 (1959). Using the same geometries assumed for the analogous aluminum(III)–fluoride species in making the symmetry number correction, one obtains $\Delta S_{\mathrm{cor}} = 7 - 3\Delta Z^2$ for the scandium(III)–fluoride reactions at 25° in perchlorate solutions of ionic strength equal to 0.5 *M*.

[9] D. B. Scaife and H. J. V. Tyrrell, *J. Chem. Soc.*, 394 (1958).

[10] W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 1548 (1953).

[11] K. Schug and E. L. King, *ibid.*, **80**, 1089 (1958).

[12] C. H. Shomate and E. H. Huffman, *ibid.*, **65**, 1625 (1943).

[13] "Selected Values of Chemical Thermodynamic Properties," Circular No. 500, National Bureau of Standards, p. 487.

mercury(II) of 0.05 *M* in the presence of lithium ion, sodium ion, magnesium ion and barium ion were, in kcal./(mole of Hg^{II}), −0.8, −1.0, -0.8_8 and −1.1, respectively. The experimental values of $\Delta H_2'$, which is equal to $\{\Delta H_1 + \Delta H_2\}$, corrected for the heat of dilution, in the presence of lithium ion, sodium ion, magnesium ion and barium ion, were, in kcal./mole, -12.6_1, -12.4_8, -12.5_4 and -12.8_9, respectively. These figures compared directly with those for experiments 9–13 in Table I indicate that the value of ΔH for reaction 2′ shows no appreciable dependence upon the nature of the predominant cation in the solution. In the interpretation of most of the experiments in the present work it was necessary to assume that changing the anion which is the principal contributor to the ionic strength has no influence upon the values of ΔH_n (n = 1 to 4). This assumption, which cannot be checked directly, is given only mild support by the results described in this section.

Experiments in which Hydrochloric Acid Solution was Added to Mercury(II) Perchlorate–Perchloric Acid Solution.—In each of four experiments, a sample of 1.86 to 10.8 ml. of 5.98 *M* hydrochloric acid was added to 300 ml. of a perchloric acid solution containing mercury(II) perchlorate; the final ionic strength of the solution was 0.50 ± 0.05 *M*. The heat of dilution of 5.98 *M* hydrochloric acid to 0.1–0.2 *M* in a solution with $I = 0.5$ *M* was found to be $-1.53_6 \pm 0.02$ kcal./mole. In these experiments in which hydrochloric acid is added to mercury(II) from 20 to 60% of the observed evolved heat was due to the heat of dilution. The results of these experiments are given in Table II.

TABLE II

THE HEAT EVOLVED UPON ADDING HYDROCHLORIC ACID TO MERCURY(II) PERCHLORATE–PERCHLORIC ACID SOLUTION

$T = 25.0 \pm 0.2°$ $I = 0.50 \pm 0.05$ *M*

Exp.	Mercury(II) (mmole)	$[Cl^-]$	$\bar{n}$	Heat evolved (kcal./mole Hg^{II}) Obsd.[a]	Calcd.[b]
20	11.10	2.46×10^{-7}	1.00	6.37	6.2
21	5.55	1.0×10^{-4}	2.00	12.62	12.8
22	5.22	1.25×10^{-1}	3.16	14.40	14.4
23	4.44	1.75×10^{-1}	3.36	14.60	14.6

[a] Corrected for the heat of dilution of hydrochloric acid into perchloric acid solution. [b] Calculated using the ΔH_n values given in Table V.

Experiments in which Solid Mercury(II) Chloride was added to Hydrochloric Acid Solution.—Eight experiments were run in which solid mercury(II) chloride was added to hydrochloric acid solution. The heat of solution of crystalline mercury(II) chloride in the absence of the effects of additional complexing by more chloride ion was determined by substituting perchloric acid for hydrochloric acid. The results of these experiments are summarized in Table III.

TABLE III

THE HEAT EFFECTS ASSOCIATED WITH THE SOLUTION OF CRYSTALLINE MERCURY(II) CHLORIDE IN ACIDIC SOLUTION[a,b] ($T = 25.0 \pm 0.2°$)

Acid, *M*	Perchloric acid Heat absorbed (kcal./mole Hg^{II})	Hydrochloric acid Heat absorbed (kcal./mole Hg^{II})
0.5	3.63	1.67
1.0	3.34	1.22
2.0	3.02	0.68
4.0	2.47	0.00

[a] The experiments at 4.0 *M* $HClO_4$ involved 0.4 to 0.7 g. $HgCl_2$; all others involved 1.7 to 3.5 g. $HgCl_2$. [b] Each entry in table is the average of two experiments; the average difference between the pairs which were averaged was 0.06 kcal./mole of Hg^{II}.

The value of ΔH for the solution of mercury(II) chloride in pure water at 25° obtained from the temperature coefficient of the solubility[14] is +3.2 kcal./mole. Only the experiments at 0.5 *M* acid can be compared with the results of the experiments reported in Tables I and II. The net heat evolved in 0.5 *M* hydrochloric acid is 1.9_6 kcal./mole Hg^{II}. (Using the values of ΔH_3^0 and ΔH_4^0 to be given in Table V, one calculates an expected evolution of heat of 2.0 kcal./mole Hg^{II} for these experiments.)

Experiments in which Mercury(II) Perchlorate was Added to Bromide or Iodide Solution.—Three experiments were performed on the mercury(II)-bromide system and the same number on the iodide system. In each case the calorimeter contained 0.50 *M* sodium halide. Under these circumstances the mercury(II) is present in the final solution predominantly as tetrabromo- or tetraiodo-mercury(II) ion. The final concentration of halide ion was calculated using the relevant equilibrium quotient values. The experiments are summarized in Table IV.

TABLE IV

THE HEAT EVOLVED UPON ADDING MERCURY(II) PERCHLORATE TO SODIUM BROMIDE OR SODIUM IODIDE SOLUTION[a]

$T = 25.0 \pm 0.2°$ $I = 0.50 \pm 0.05$ *M*

Mercury(II) (mmole)	$[Br^-]$	$[I^-]$	Heat evolved[b] (kcal./mole Hg^{II})
9.25	0.464	...	27.8
3.70[c]	0.485	...	28.2, 28.0
3.70[d]	...	0.485	45.0, 44.3, 44.7

[a] In these experiments, the total volume of the solution in the calorimeter was 350–360 ml. [b] Corrected for the heat of dilution of the stock solution of mercury(II) perchlorate into a solution with I = 0.50 mole/l., perchloric acid being the principal contributor to the ionic strength. [c] Two identical experiments. [d] Three identical experiments.

Discussion

The data presented in Tables I and II have been used to calculate the values of ΔH_n^0 (n = 1 to 4) for the mercury(II)–chloride reactions. The distribution of the mercury(II) among the five forms in which it existed in the final solution in each experiment was calculated using the stoichiometric composition and the Q_n values. The value of $(\Delta H_1^0 + \Delta H_2^0)$ came directly from experiments 9 to 13 in which the final solutions had $\bar{n}$ = 2.00 and contained very predominantly dichloromercury(II). The sum of ΔH_1^0 and ΔH_2^0 then was resolved by experiments 1 to 8 and 20, the final solutions in which contained between 30 and 40% monochloromercury(II) ion and between 9 and 60% dichloromercury(II). The values of ΔH_3^0 and ΔH_4^0 came from the simultaneous consideration of experiments 14 to 19, 22, and 23; the relative amounts of the mercury(II) present as trichloromercury(II) ion and tetrachloromercury(II) ion in the final solutions in these experiments ranged from 17 to 31% and from 12 to 78%, respectively. These derived values of ΔH_n^0 are presented in Table V.

It is to be noted that each of the first two stepwise reactions is quite exothermic. On the basis of the values of ΔH^0, one would conclude that the first two reactions are similar in nature; each probably involves the replacement of one water molecule by one chloride ion with no change in configuration. The slight difference in the values of ΔH_1^0 and ΔH_2^0 is probably a solvation energy effect. The third and fourth stepwise reactions are much less exothermic. It would appear that in each of these reactions something more occurs than simply the replacement of one water molecule by one chloride ion.

Perhaps the relative values of ΔS^0 for the reactions will shed some light on the nature of these reactions. (The absolute values of ΔS^0 are not of interest since these reactions have $\Delta n \neq 0$, where Δn

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(14) R. D. Eddy and A. W. C. Menzies, *J. Phys. Chem.*, **44**, 207 (1940).

TABLE V

VALUES OF ΔH^0 AND ΔS^0 AT 25° AND $I = 0.50\ M$ FOR MERCURY(II)–HALIDE REACTIONS

$HgCl_{n-1}^{+3-n} + Cl^- = HgCl_n^{+2-n}$

n	Q^a	ΔH^0, kcal.^{b}	ΔS^0, e.u.
1	5.5×10^6	−5.9	+11.1
2	3.0×10^6	−6.9	+ 6.3
3	8.9	−2.2	− 3.0
4	11.2	+0.1	+ 5.1
$Hg^{++} + 4X^- = HgX_4^=$			
$X^- = Cl^-$	1.64×10^{15}	−14.9	+19.5
$X^- = Br^-$	8.9×10^{20}	−27.7	+ 3.0
$X^- = I^-$	7.2×10^{29}	−44.3	−13.4

[a] For the chloride system the values of Q_1 and Q_2 are those determined by Sillen[6a]; the values of Q_3 and Q_4 are those determined by Marcus.[6b] The value of Q_4' for the chloride reaction is the product of the values of Q_1, Q_2, Q_3 and Q_4 given above. For the bromide reaction, the value of Q_4' is the average of the values given by Sillen[6a] and Marcus[6b]; for the iodide reaction, the value of Q_4' is that given by Marcus.[6b] [b] van Panthaleon van Eck[3b] has obtained −2.5 kcal. for ΔH_3^0 and −0.6 kcal. for ΔH_4^0; from existing thermal data, he calculates −13.3 for ($\Delta H_1^0 + \Delta H_2^0$). These values and those reported here agree within the experimental uncertainties.

is the difference between the number of solute particles on the product and reactant side of the chemical equation, and the numerical values of ΔS_n^0 depend, therefore, upon the choice of concentration scale.) Before a sound comparison of the values of ΔS^0 can be made, they should be corrected for the contribution of the symmetry number factor, $\Delta S^0_{cor} = \Delta S^0 + R \ln \sigma_P/\sigma_R$, where σ_P and σ_R are the symmetry numbers of the product and reactant mercury(II) species, respectively. If it is assumed that the first two chloride ions added replace two water molecules held in a linear O–Hg–O arrangement, the values of ΔS^0_{cor} for reactions 1 and 2 are $9._7$ e.u. and $7._7$ e.u., respectively. This gives a b value of $1._0$ if one assumes that the values of ΔS_{cor}^0 for reactions 1 and 2 are correlated by equation 1. This value of b is smaller than the values for the fluoride-complexing reactions,[7b,8] which is not unreasonable in view of the larger size of the ions involved in the mercury(II)–chloride reactions.

For the purposes of probing the nature of trichloromercury(II) ion and tetrachloromercury(II) ion, values of $\Delta S^0_{3,cor}$ and $\Delta S^0_{4,cor}$ were calculated using equation 1 fit to $\Delta S^0_{1,cor}$ and $\Delta S^0_{2,cor}$ with $b = 1.0$, which fits perfectly, and $b = 2.0$, an arbitrarily chosen alternate value. A summary of the corrected entropy change values so calculated is given in Table VI. These values are to be compared with the experimental values, both before and after correction for the symmetry number factor. A comparison of the uncorrected experimental values with those calculated using either equation indicates that the value of ΔS_3^0 is too negative and the value of ΔS_4^0 is too positive. In making the symmetry number corrections, a tetrahedral configuration for tetrachloromercury(II) ion has been assumed; this has been suggested by its Raman spectrum[15] as well as by the X-ray diffraction measurements already cited.[3] For dichloromercury(II) and trichloromercury(II) ion values of σ equa to 2 and 6, respectively, have been chosen. The choice of 6 for trichloromercury(II) ion was dictated as much by the fact that this extreme of the possible values will tend to reduce the abnormality of the values of $\Delta S^0_{3,cor}$ and $\Delta S^0_{4,cor}$ as it was by any notion that trichloromercury(II) ion is planar. The values of ΔS^0_{cor} for reactions 3 and 4 show the same discrepancy from the values calculated using equation 1 as did the uncorrected experimental values. The conclusion that the value of ΔS_3^0 is abnormally negative and the value of ΔS_4^0 is abnormally positive stands. In the rearrangement which occurs in reaction 3, there is some tightening of the hold on water molecules by mercury(II). In reaction 4, on the other hand, there appears to be a loosening of the hold on water molecules by mercury(II). Perhaps reaction 4 is correctly represented as

TABLE VI

THE ENTROPY CHANGES IN REACTIONS 3 AND 4

Reaction	ΔS^0(e.u.)	ΔS^0cor, calcd. (eq. 1) 1^a	2^b	ΔS^0cor. = $\Delta S^0 + R \ln \sigma_P/\sigma_R$, exp. value
3	−3.0	5.7	2.7	-0.8^c
4	+5.1	3.7	−1.3	$+6.5^d$

[a] Calcd. using $\Delta S^0_{cor} = 5.7 - 1.0\ \Delta Z^2$. [b] Calcd. using $\Delta S^0_{cor} = 2.7 - 2.0\ \Delta Z^2$. [c] Calcd. using $\sigma_{HgCl_2} = 2$ and $\sigma_{HgCl_3^-} = 6$, the extreme values which make $\Delta S_3{}^0_{cor}$ as positive as possible. [d] Calculated using $\sigma_{HgCl_3^-} = 6$ and $\sigma_{HgCl_4^=} = 12$. This choice of $\sigma_{HgCl_3^-}$ is the maximum possible value, which will make ΔS^0_{4cor}, as negative as possible.

$$Hg(OH_2)_3Cl_3^- + Cl^- = HgCl_4^= + 3H_2O$$

The addition of one chloride ion with the liberation of three water molecules would result in an abnormally positive value of ΔS^0. The value of ΔH_4^0 also lends some support to this picture; the fact that three water molecules are set free and only one chloride ion becomes coördinated would tend to make the reaction less exothermic.

The entropy changes in the mercury(II)–chloride complex ion reactions contribute relevant information on the interaction of the mercury(II) species with the solvent. Another source of such information is the relationship between the entropy and enthalpy of vaporization of neutral dichloromercury(II). Associated with the process

$$HgCl_2 \text{ (aq., hyp. 1 } m) = HgCl_2 \text{ (g., 1 atm.)}$$

at 298° are values of ΔH^0 and ΔS^0 of 16.7 kcal. and + 27 e.u., respectively.[16] The point for mercury(II) chloride in a plot of ΔS^0_{vap} *versus* ΔH^0_{vap} (*e.g.* Fig. 3 in the paper by Frank and Evans[17]) falls very close to the normal Barclay–Butler line for non-aqueous solutions ($\Delta S^0_{vap} = 6.5 + 1.1\ \Delta H^0_{vap}$; the values of the parameters are appropriate for the solution phase and vapor phase concentrations already used) and thus corresponds to an abnormally negative value of ΔS^0_{vap} compared to the value shown by most non-ionic solutes in water.[17] In this respect, $HgCl_2$ in water resembles a water solution of the polar solute NH_3 and water itself which also

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(15) J. A. Rolfe, D. E. Sheppard and L. A. Woodward, *Trans. Faraday Soc.*, **50**, 1275 (1954). The evidence for a tetrahedral $MX_4^=$ is much stronger in the case of $CdI_4^=$ than in the case of $HgCl_4^=$, for which but a single Raman line has been observed.

(16) The values were obtained by combining the data on the solubility and heat of solution of $HgCl_2$(c) in water (ref. 14) with data on the vapor pressure of the crystalline solid as a function of temperature (R. Ruf and W. D. Treadwell, *Helv. Chim. Acta*, **37**, 1941 (1954)).

(17) H. S. Frank and M. V. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

have values of ΔH^0_{vap} and ΔS^0_{vap} agreeing reasonably well with the Barclay–Butler equation.[18] Certainly ammonia and water both interact strongly with water and the present comparison suggests that $HgCl_2$ also does. In this connection, it is to be noted that Allen and Warhurst,[19] in their correlation with dielectric constant of the frequency of the Raman line associated with the symmetrical vibration of $HgCl_2$ in various solvents, did not feel compelled to suggest specific bonding between $HgCl_2$ and water; of the solvents they studied, only pyridine and dioxane were suggested to form bonds of appreciable strength with $HgCl_2$. Their results were, however, taken to indicate a stronger interaction of the polar Hg–Cl bonds with water than exists with many solvents of lower dielectric constants (*e.g.*, benzene, certain esters, certain alcohols, acetone and acetonitriles).

The Latimer and Jolly approach[10] to the prediction of ΔS^0 values for complex ion formation reactions has not been tested adequately for reactions involving charged ligands, for in such cases the manner in which the "charge effect" should be handled has not been solved. Latimer and Jolly consider the "charge effect" to be small, but the evidence they cite for this is marred by their consideration of reactions with $\Delta n \neq 0$. By combining the values of ΔS^0 for certain reactions studied in the present work and in the mercury(II)–bromide studies of Scaife and Tyrrell[9,20] one can check, using reactions with $\Delta n = 0$, the Latimer and Jolly prediction regarding reactions involving complexes with charged ligands but in which the value of ΔZ^2 is zero. These reactions are

$$Br^- + \frac{1}{a}\,HgCl_a^{+2-a} = Cl^- + \frac{1}{a}\,HgBr_a^{+2-a}$$

with $a = 2, 3$ and 4, and

$$I^- + {}^1/_4HgCl_4^{=} = Cl^- + {}^1/_4HgI_4^{=}$$

The Latimer and Jolly approach predicts ΔS^0 values of -3.3 e.u. for the bromide reactions and -7.4 e.u. for the iodide reaction.[21] The experimental values are -5.2, -4.2 and -4.2 e.u. for the bromide reactions with $a = 2, 3$ and 4, respectively, and -8.3 e.u. for the iodide reaction. The agreement is probably within the total uncertainty, that of the experimental values of ΔS^0 and of the experimentally determined quantities which went into the predicted values. (Since the value of ΔZ^2 for each reaction is zero, it is expected that the value of ΔS^0 will be approximately independent of I between $I = 0.5$ and $I = 0$.) The correlation is good enough in any case to suggest that the mercury(II)–bromide and mercury(II)–iodide species involved have the same coördination number as the corresponding mercury(II)–chloride species.[22]

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[18] Professor H. S. Frank pointed this out to us.

[19] G. Allen and E. Warhurst, *Trans. Faraday Soc.*, **54**, 1786 (1958).

[20] The values of ΔS^0 for reactions 3 and 4 in the bromide series at $I = 0.5$ M are -0.5 and ~ 0 e.u., respectively.

[21] In making the predictions, the entropy values used were: $\bar{S}^0_{Cl^-} = 13.2$, $\bar{S}^0_{Br^-} = 19.3$, $\bar{S}^0_{I^-} = 26.1$, $S_{Cl^-(bound)} = 8.1$, $S_{Br^-(bound)} = 10.9$ and $S_{I^-(bound)} = 13.6$ e.u. (These values were taken from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice–Hall, Inc., New York, N. Y., 1952).

[22] ADDED IN PROOF.—Scaife and Tyrrell[9] have suggested, however, that tribromomercury(II) ion is the tetrahedral species $Hg(OH_2)Br_3^-$

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, UNIVERSITY PARK, LOS ANGELES, CALIFORNIA]

Trifluoromethyl-bromo-phosphines and Phosphoranes[1]

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The removal of CF_3 groups from phosphorus(III) by the action of bromine is understood in terms of formation of the phosphoranes $(CF_3)_nPBr_{5-n}$, which lose CF_3Br in reverting to phosphorus(III) compounds. A number of intermediate and parallel processes are recognizable. The transfer of Br_2 from $(CF_3)_3PBr_2$ to $(CF_3)_2PBr$, from $(CF_3)_2PBr_3$ to CF_3PBr_2 and from CF_3PBr_4 to PBr_3 correlates with greater stability for phosphoranes having more Br and fewer CF_3 groups.

The cleavage of the P–CF_3 bond by halogens has been known for some time; for example the biphosphine $P_2(CF_3)_4$ heated with excess iodine or bromine eventually yields all of the CF_3 groups as CF_3I or CF_3Br, or $(CF_3)_3P$ with I_2 gives CF_3I, $(CF_3)_2PI$, CF_3PI_2 and PI_3.[2] However, these reactions have been carried on only at relatively high temperatures and little has been known of their intermediate stages.

Our initial studies of the $P_2(CF_3)_4$–Br_2 reaction indicated the formation of the phosphorane $(CF_3)_2PBr_3$ and suggested that the loss of CF_3Br from this and other phosphoranes might be the chief mechanism for removing the highly electronegative CF_3 group from its bond to phosphorus. This bromine reaction seemed best for further study, since iodophosphoranes cannot be prepared at convenient temperatures, if at all, and chlorophosphoranes tend to be either too stable—*e.g.*, CF_3PCl_4[3]—or explosive under certain conditions—*e.g.*, $(CF_3)_3PCl_2$.[2] However, the intermediate bromophosphoranes proved to be both recognizable and subject to decomposition under mild conditions.

The first step of the action of bromine upon $P_2(CF_3)_4$ is the virtually quantitative P–P bond cleavage

$$(CF_3)_2P\text{–}P(CF_3)_2 + Br_2 \longrightarrow 2(CF_3)_2PBr \qquad (1)$$

This is followed by the almost quantitative conver-

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[2] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.* 1565 (1953).

[3] W. Mahler and A. B. Burg, THIS JOURNAL, **80**, 6161 (1958).