# Thermodynamic Properties of Thallium(III) Chloride and Bromide Complexes in Aqueous Solution

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The changes in enthalpy for the formation of complexes of thallium(III) with chloride and bromide have been determined. All data (Table 2) refer to a medium of 3 M HClO₄ + 1 M NaClO₄ and a temperature of 25.00°C.

The best method of obtaining accurate thermodynamic functions for complex formations seems to be a potentiometric determination of the various stability constants followed by a calorimetric determination of the corresponding enthalpy changes. The stability constants used here are those determined by Ahrland *et al.*[1] The calorimeter and the calorimetric titration procedure have been developed by Gerding *et al.*[2]

At the calorimetric titrations 100 ml of a solution S, containing $C_M$ M thallium(III) perchlorate, was titrated with increasing volumes, $v$ ml, $(0 < v < 26)$ of a solution T, containing $C_A$ M NaA, where A = Cl or Br. In order to maintain a constant ionic strength and avoid hydrolysis both S and T contained sodium perchlorate and perchloric acid with the concentrations $C_{NaClO_4}$ and $C_{HClO_4}$ M, respectively. Two sets of titrations were performed, in which S and T had the following compositions:

I.  S: $C_M = 9.74 \times 10^{-3}$, $C_{HClO_4} = 3.00$, $C_{NaClO_4} = 0.94$.

T: $C_{NaA} = 0.200$, $C_{HClO_4} = 3.00$, $C_{NaClO_4} = 0.80$.

II.  S: $C_M = 1.95 \times 10^{-3}$, $C_{HClO_4} = 3.00$, $C_{NaClO_4} = 0.99$.

T: $C_{NaA} = 0.040$, $C_{HClO_4} = 3.00$, $C_{NaClO_4} = 0.96$.

The results are shown in Table 1. Each value given there is the average of two independent measurements.

The heat change, $Q$ cal, after each addition of titrant was measured with an uncertainty of $\pm$ 0.02 cal by the use of a thermistor. During the initial and final period before and after each new addition of T, the resistance of the thermistor was measured for a period of time, needed for a change of resistance

*Table 1.* Heat evolved at the titrations of thallium(III) bromide to the left and chloride to the right. Titration set I in the upper part, set II in the lower part of the table.

| $v$ ml | $Q_{exp}$ cal | $Q_{calc}$ cal | $Q_{exp}$ cal | $Q_{calc}$ cal |
|---|---|---|---|---|
| 2.01 | $3.58_5$ | 3.60 | $2.37_4$ | 2.42 |
| 4.02 | $3.53_9$ | 3.55 | $2.36_1$ | 2.35 |
| 6.03 | $2.92_9$ | 2.95 | $2.01_4$ | 1.99 |
| 8.04 | $2.46_6$ | 2.46 | $1.70_4$ | 1 67 |
| 10.05 | $2.29_9$ | 2.28 | $1.32_2$ | 1.36 |
| 12.05 | $1.92_5$ | 1.88 | $0.46_6$ | 0.46 |
| 14.06 | $1.67_5$ | 1.65 | $0.31_3$ | 0.30 |
| 16.07 | $1.20_6$ | 1.24 | $0.20_0$ | 0.21 |
| 18.08 | $0.91_0$ | 0.93 | $0.10_8$ | 0.14 |
| 20.09 | $0.51_1$ | 0.55 | $0.11_6$ | 0.07 |
| 22.1 | $0.18_8$ | 0.12 | | |
| 24.1 | $0.03_0$ | 0.00 | | |
| 26.1 | $0.03_0$ | 0.00 | | |
| 1.00 | $0.36_4$ | 0.36 | $0.24_0$ | 0.24 |
| 3.01 | $0.71_2$ | 0.72 | $0.48_9$ | 0.48 |
| 5.02 | $0.66_5$ | 0.67 | $0.44_0$ | 0.44 |
| 7.03 | $0.49_1$ | 0.51 | $0.34_9$ | 0.35 |
| 9.04 | $0.49_2$ | 0.48 | $0.31_7$ | 0.32 |

of 0.2 ohm. A plot of resistance *versus* time showed a linear relationship. For our small temperature changes the slopes of these lines were approximately the same for the initial and final periods. The change of the resistance corresponding to the heat evolved at each titration step was taken as the difference between the ordinates of these two lines at a time, chosen 15 sec after the pipette bulb in the calorimeter had been halfemptied.

The calorimeter was calibrated electrically to determine the heat equivalent, $\varepsilon_v$ cal ohm$^{-1}$ of the systems. For all solutions S and T used here, the experimental results may be described by the equation.

$$\varepsilon_v = 1.89_1 + 0.018_9 \, v \tag{1}$$

With an accuracy better than $5 \times 10^{-3}$ cal ohm$^{-1}$ in the range $0 < v < 20$. The heats of dilution for the solutions of ligands and of thallium(III) were found to be zero within the experimental errors.

*Chemicals.* A thallium(III) perchlorate solution was prepared by anodic oxidation of thallium(I) perchlorate in 3 M perchloric acid.[3] Thallium(I) perchlorate was obtained by dissolving thallium(I) carbonate (Merck, *p.a.*) in perchloric acid. Sodium perchlorate was prepared by neutralizing perchloric acid with sodium carbonate. From the neutral solution crystals formed between 80°C and 135°C were separated and dried at 140°C. Sodium bromide (Baker, *p.a.*) and sodium chloride (Merck, *p.a.*) were used without purification.

The thallium(III) perchlorate was standardized by iodate titration after reduction with sulphur dioxide. No thallium(I) was found in the thallium(III) solution by direct iodate titrations.

## TREATMENT OF THE DATA

The heat, $Q$ cal, evolved after each addition in the titration, is given in Table 1. It has been obtained by multiplying the corresponding value of $\varepsilon_v$ with the change of the resistance for the titration step in question. The computation of the enthalpy change, $\Delta H_j^\circ$ kcal/mole, for the reaction:

$$TlA_{j-1}^{4-j} + A^- \rightleftharpoons TlA_j^{3-j} \qquad (I)$$

has been computed by a high speed computer (IBM 7090) with the least square program Letagrop Kalle developed by Sillén et al.[4] and also by a simple graphical method. In both cases the equilibrium constants by Ahrland et al.[1] have been used to compute the composition of the solution. These constants

$$\beta_n = \frac{TlA_n^{3-n}}{[Tl^{3+}][A^-]^n} \qquad (2)$$

are given below in $M^{-n}$ for the thallium(III) bromide to the left and for the chloride to the right:

$$\beta_1 = (4.2 \pm 0.1) \times 10^9 \qquad \beta_1 = (3.5 \pm 0.3) \times 10^7$$
$$\beta_2 = (1.16 \pm 0.05) \times 10^{17} \qquad \beta_2 = (2.4 \pm 0.2) \times 10^{13}$$
$$\beta_3 = (3.9 \pm 0.3) \times 10^{22} \qquad \beta_3 = (6.2 \pm 0.5) \times 10^{16}$$
$$\beta_4 = (5.4 \pm 0.2) \times 10^{26} \qquad \beta_4 = (3.8 \pm 0.4) \times 10^{19}$$

They are valid in 3 M $HClO_4$ + 1 M $NaClO_4$ at 20°C, so they have to be recalculated to 25°C. This can be done by an iterative process, starting with the constants above as a first approximation of the values for 25°C. This will give a first set of enthalpy values, which can then be used to correct the equilibrium constants by the equation:

$$\frac{d \ln\beta_n}{d T} = \frac{\sum\limits_{j=1}^{n} \Delta H_j^\circ}{RT^2} \qquad (3)$$

From these better approximations of the constants at 25°C new enthalpy values are computed and so on.

The graphical method has been the following (cf. Rossotti and Rossotti,[5] and Grenthe [6]): The molar heat change, $\Delta h$ kcal mole$^{-1}$, when $v$ ml of solution T has been added to 100 ml of solution S, is defined by

$$\Delta h = -\frac{Q_{\text{sum}}}{C_M (100 + v)} \qquad (4)$$

where $Q_{\text{sum}}$ cal is the sum of the heats evolved after each addition of T.

If the stability constants are known, the function $\gamma_1$ below can be computed from the experimental values of $\Delta h$ above.

$$\gamma_1 = \frac{\Delta h(1 + \sum\limits_{j=1}^{4} \beta_j[A^-]^j)}{[A^-]} \qquad (5)$$

It may easily be shown that $\gamma_1$ is a polynom function of $[A^-]$, viz.

$$\gamma_1 = \sum_{n=1}^{4} K_n [A^-]^{n-1} \tag{6}$$

where

$$K_n = \beta_n \times \sum_{j=1}^{n} \Delta H_j^{\circ} \tag{7}$$

Hence

$$\lim_{[A^-] \to 0} \gamma_1 = \beta_1 \times \Delta H_1^{\circ} \tag{8}$$

so $\beta_1 \times \Delta H_1^{\circ}$ is obtained by extrapolation. All the values of $\beta_n \times \sum_{j=1}^{n} \Delta H_j^{\circ}$ can then be determined correspondingly by extrapolation of suitable functions,

$$\gamma_2 = \frac{\gamma_1 - \beta_1 \Delta H_1^{\circ}}{[A^-]} \quad (= \sum_{n=2}^{4} K_n [A^-]^{n-2}) \tag{9}$$

and so forth.

In the computations above the concentration of free ligand has to be known. It is easily obtained from the values of $C_M$, $C_A$, and $\beta_n$ by wellknown graphical methods or more rapidly by a high speed computer. Eqns. (6) and (7) show that $\Delta h$ is a function only of the free ligand concentration. This is so, because no polynuclear complexes have been introduced in the calculations. If such complexes exist $\Delta h$ becomes dependent also on $C_M$.

Fig. 1 shows that $\Delta h$ is independent of $C_M$, so polynuclear species are not needed to describe our results. In this figure the average number, $\bar{n}$, of ligands per central atom has been chosen as abscissa

$$\bar{n} = \frac{\sum_{j=1}^{4} j\beta_j [A^-]^j}{1 + \sum_{j=1}^{4} \beta_j [A^-]^j} \tag{10}$$

instead of the ligand concentration itself. Since both $\bar{n}$ and $\Delta h$ are functions only of $[A^-]$ in a mononuclear system, points from titration series with different values of $C_M$ shall fall on the same curve. A representation like that in Fig. 1 shows directly, how the enthalpy changes as the complex formation proceeds in the two systems.

Table 2 contains the enthalpy values obtained together with the change of the standard free energy $\Delta G_j^{\circ}$ kcal/mole and entropy $\Delta S_j^{\circ}$ cal/mole degree for the stepwise reactions at 25°C. They are calculated from the equations:

$$\Delta G_j^{\circ} = -RT \ln \frac{\beta_j}{\beta_{j-1}} \tag{11}$$

and

$$\Delta H_j^{\circ} = \Delta G_j^{\circ} + T \Delta S_j^{\circ} \times 10^{-3} \tag{12}$$

For the enthalpy values the standard deviation from the least square computations is also given. From the values of $\Delta H_j^{\circ}$ and $\beta_j$ the heat $Q_{calc}$ has been com-

puted by the aid of eqns. (7), (6), (5,) and (4) and has been compared with the experimental values of $Q$ in Table 1. Most of the differrences between $Q_{calc}$ and $Q_{exp}$ lie within the expected error of 0.02 cal. The uncertainty of the free energy values has been judged from the accuracy of Ahrland's graphic computation [1] of the stability constants.

Besides the determination of the thermodynamic functions this calorimetric study has also given some information about thallium chloride and bromide systems, which is not so easily obtained by other methods. (i) The data of Fig. 1 indicate that the systems are mononuclear. (ii) As can be seen from
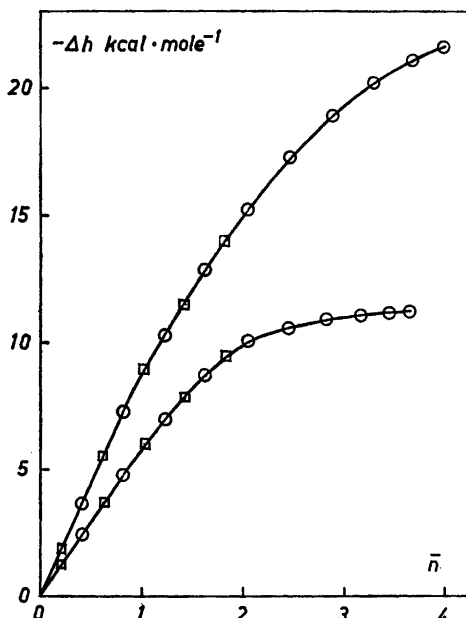


Fig. 1. The molar enthalpy change $\Delta h$ for the reaction between thallium(III) and bromide (upper curve) and chloride (lower curve) as a function of the average ligand number $\bar{n}$ for two values of the thallium(III) concentration, viz. 9.75 mM, O, and 1.95 mM, □.

Table 1 the titration with bromide has been continued after the point of equivalence (at $C_A = 4C_M$, i.e. $v \sim 20$). From the table it is quite evident that there is practically no heat evolved when $v > 20$. This indicates

Table 2. $\Delta H_j^\circ$, $\Delta G_j^\circ$ and $\Delta S_j^\circ$ for the reaction $TlA_{j-1}^{4-j} + A^- \rightleftharpoons TlA_j^{3-j}$ at 25°C. A = Br to the left; A = Cl to the right. Ionic medium 3 M $HClO_4$ + 1 M $NaClO_4$.

| $j$ | $-\Delta G_j^\circ$ kcal/mole | $-\Delta H_j^\circ$ kcal/mole | $\Delta S_j^\circ$ cal/mole degree | $-\Delta G_j^\circ$ kcal/mole | $-\Delta H_j^\circ$ kcal/mole | $\Delta S_j^\circ$ cal/mole degree |
|---|---|---|---|---|---|---|
| 1 | 12.96 ± 0.02 | 8.96 ± 0.02 | 13.4 ± 0.2 | 10.22 ± 0.06 | 6.04 ± 0.03 | 13.9 ± 0.3 |
| 2 | 10.05 ± 0.04 | 6.09 ± 0.05 | 13.3 ± 0.3 | 7.88 ± 0.1 | 4.05 ± 0.03 | 12.9 ± 0.4 |
| 3 | 7.42 ± 0.08 | 4.58 ± 0.07 | 9.7 ± 0.5 | 4.63 ± 0.1 | 1.08 ± 0.08 | 11 9 ± 0.6 |
| 4 | 5.62 ± 0.07 | 2.14 ± 0.08 | 11.7 ± 0.5 | 3.79 ± 0.1 | 0.17 ± 0.07 | 12.2 ± 0.6 |

strongly that no more than 4 bromide ions can be bound by a thallium(III) ion. This conclusion can be drawn, even if $\Delta H_5 \sim 0$. For, if a fifth complex should have been built up, the complex formation would not have finished suddenly at $v = 20$. A further complex formation should then have given a gradual decrease of the heat evolved and not a sudden stop. Our data favour Ahrland's opinion [1] that the coordination number of thallium(III) is four in these systems. If a fifth or sixth complex is formed, as has been proposed by Peschanski and Valladas-Dubois,[7] this could only occur after a considerable „stop" in the $\bar{n}$-curve at $\bar{n} = 4$. The equilibrium constants given by these authors do not give such a stop.

A remarkable feature of these systems is the almost constant entropy change for all the eight reactions summarized in Table 2.

*Note added in proof.* In a recent paper (this journal **18** (1964) 307) Gwyneth Nord and Ulstrup have computed a value of $-\Delta H_4^\circ = 5.1 \pm 0.6$ (kcal mole$^{-1}$) from the temperature dependence of $\Delta G_4^\circ$. The free energy was determined by extraction of thallium(III) chloride with isopropyl ether. The same method has been used by R. W. Dodson, Brookhaven National Laboratory, U.S.A. (personal communication to Dr. S. Ahrland at our laboratory). He found $\Delta G_4^\circ$ (and $\Delta G_3^\circ$) to be rather independent of temperature. This is consistent with our numerically small value of $\Delta H_4^\circ$ (and $\Delta H_3^\circ$?).

## REFERENCES

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