

The Stability of Metal Halide Complexes in Aqueous Solution

VI. Further Investigation on the Chloride and Bromide Complexes of Thallium(III)

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The complex formation of Tl^{3+} with Cl^- and Br^- has been studied by various methods. The measurements have been performed at $20^\circ C$ in a medium of the acidity 3 M and the ionic strength 4 M.

Investigations already reported¹ indicate strongly that only four mononuclear complexes are formed. This conclusion has now been confirmed by measurements of the solubility of AgCl and AgBr in chloride and bromide solutions also containing Tl(III). A solubility column, similar to that described by Dyrssen,² was used.

For low chloride concentrations, the complex formation function found from the Tl(III)/Tl(I) measurements has also been verified by the use of the Ag/AgCl electrode. For high chloride concentrations, on the other hand, this electrode has been shown to give erroneous results. The calorimetric measurements of Leden and Ryhl³ are also consistent with a maximum coordination of four Cl^- or Br^- around Tl^{3+} .

The results of the central ion measurements by means of the Tl(III)/Tl(I) electrode, reported previously,¹ are thought to be reliable as the electrode seemed to work very well. The calculations show that only the first four mononuclear complexes are formed between Tl^{3+} and Cl^- or Br^- . At high ligand concentrations, however, the values of the ligand number, \bar{n}_M , determined as described in Ref.¹, are very sensitive to small deviations in the measured potentials. In fact they tend to come out improbably high (Ref.¹, Tables 4, and 6, Fig. 6a). These values have certainly no physical meaning and have not been used in the calculations of the stability constants of Ref.¹

From the same measurements, however, \bar{n}_M can also be computed in another way which is not subject to the errors mentioned, *viz.* by means of the Bodländer equation (*cf.* Leden⁴). Such a computation has now been performed and the result is reported below.

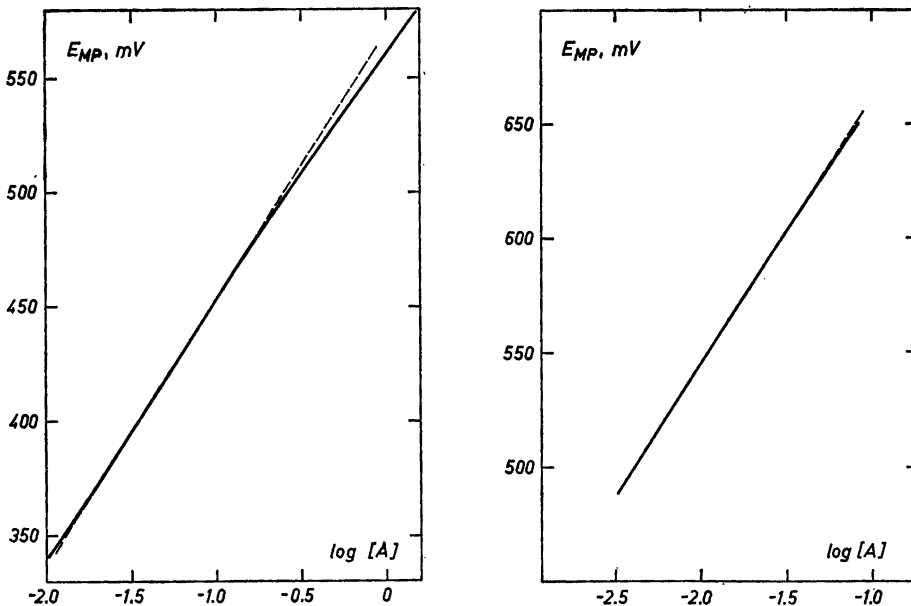
It may be argued, however, that corresponding values of \bar{n}_M and the free ligand concentration $[A]$ can anyhow be found only in a rather indirect way

from the central ion measurements. It is therefore desirable to find more direct methods for the determination of these quantities.

One such method, used by several investigators,⁵⁻⁸ is the determination of $[A]$ by a silver halide electrode. For high ligand concentrations, however, the results found by this method differ considerably between various authors, and they disagree even more with those found from the Tl(III)/Tl(I) measurements. Thus the existence of six complexes is sometimes^{6,8} claimed. A critical study of this method, taking the redox conditions into special account, seems therefore desirable.

Most important, however, is to find a new method of measurement, capable of giving a definitive answer to the question about the maximum coordination number, N , of these systems. Such a method has been found, consisting in measurements of the solubility of silver chloride and bromide, respectively, in solutions containing Tl(III), besides varying concentrations of the appropriate halide ion. Under these circumstances, no oxidation reactions are possible. In order to measure very low concentrations of free chloride ions, this method has been employed before by King *et al.*⁹ in connexion with measurements by means of the Tl(III)/Tl(I) electrode. For our solubility determinations, a column similar to that described by Dyrssen,² has been used.

All measurements have been performed at 20°C, in a perchloric acid-sodium perchlorate medium of a constant ionic strength $I = 4$ M and an acidity $h = 3$ M.



Figs. 1 and 2. Fulldrawn curves give E_{MP} as a function of $\log [A]$ for the chloride (Fig. 1) and bromide (Fig. 2) systems. The dashed lines are the inflexion tangents of the curves, the slopes of which yield a maximum value of $\bar{n}_M - \bar{n}_P$ close to 4 (*cf.* p. 2128).

Table 1. Determination of \bar{n}_M by the Bodländer equation.

E_{MP} mV	$[A] \times 10^3$ M	$\bar{n}_M - \bar{n}_P$	\bar{n}_P	\bar{n}_M
Chloride				
370	19.3	3.95	0.01	3.96
400	33.5	3.98	0.03	4.01
410	41.5	3.98	0.04	4.02
420	51.0	3.98	0.05	4.03
430	63.0	3.97	0.06	4.03
460	115	3.91	0.10	4.01
490	215	3.81	0.17	3.98
520	407	3.70	0.30	4.00
540	627	3.60	0.41	4.01
560	978	3.47	0.58	4.05
570	1227	3.38	0.66	4.04
578	1483	3.28	0.76	4.04
Bromide				
520	6.1	3.98	0.01	3.99
540	9.1	3.98	0.02	4.00
560	13.5	3.98	0.03	4.01
580	20.1	3.96	0.04	4.00
600	30.3	3.94	0.06	4.00
620	44.8	3.91	0.09	4.00
640	67.5	3.88	0.13	4.01
650	82.5	3.86	0.16	4.02

DETERMINATION OF \bar{n}_M FROM THE Tl(III)/Tl(I) MEASUREMENTS BY THE BODLÄNDER EQUATION

In the present case, where the two redox states Tl(III) and Tl(I) co-exist in solution, the Bodländer equation can be written as follows (the same notation being used as in Ref.¹):

$$\frac{d E_{MP}}{d \log [A]} = \frac{RT \ln 10}{2 F} (\bar{n}_M - \bar{n}_P) \quad (1)$$

The slope of a curve E_{MP} as a function of $\log [A]$ will give the difference $(\bar{n}_M - \bar{n}_P)$. Up to fairly high values of $[A]$, \bar{n}_P is negligible compared with \bar{n}_M . Within this region E_{MP} is a linear function of $\log [A]$, once \bar{n}_M has reached its upper limit N . For very high values of $[A]$, \bar{n}_P is no longer negligible, but has to be corrected for. For this purpose values of \bar{n}_P are calculated from the constants of Nilsson.¹⁰ Though these apply to another medium, they are certainly close enough to be used for the present correction.

Figs. 1 and 2 show E_{MP} as a function of $\log [Cl^-]$ and $\log [Br^-]$, respectively, with the data taken from Ref.¹ (Tables 2, 4, and 6). Only values of $[A]$ large enough to be determined as well-defined intercepts on the C_A -axis have

been used. Inflexion tangents are drawn to show how the curves deviate from linearity. For chloride, the slope is just a little $< N$ at the lowest $[A]$ measured, then reaches a maximum $\bar{n}_M = N$, and finally decreases again as $(\bar{n}_M - \bar{n}_P)$ becomes $< N$. For bromide, the curve begins in the region where already $\bar{n}_M = N$, otherwise its course is very much the same. In Table 1, the slopes $(\bar{n}_M - \bar{n}_P)$ of Figs. 1 and 2 have been tabulated, together with the calculated values of \bar{n}_P and finally, the resulting values of \bar{n}_M . For brevity, several points of the chloride system, intermediate to those in Table 1, have been omitted.

It is evident that \bar{n}_M reaches an upper limit $N = 4$ (Table 1 yields 4.02 ± 0.04 for the chloride and 4.00 ± 0.02 for the bromide system). These values of N are also obtained as the slopes of the inflexion tangents of Figs. 1 and 2.

This result is of course no real news, just another way of expressing what is already expressed by the constancy of the functions X_4 (Ref.¹, Tables 3, 4, 5, and 6). It shows nevertheless, that reasonable values of \bar{n}_M are obtained once the systematic error inherent in the use of curves of different C_M is avoided.

It should finally be emphasized that it is of no consequence for the determination of N whether the intercepts found on extrapolation to $C_M = 0$ really yield the right values of $[A]$ (which cannot be taken for granted, as has been discussed in Ref.¹). As the curves $C_A(E_{MP})$ for various values of the parameter C_M grow parallel with increasing C_A , they will all give the same value of N irrespective of the value of $[A]$ ascribed to a certain value of E_{MP} . A modification of $[A]$ will therefore only affect the value of the constant β_4 .

SOLUBILITY MEASUREMENTS

Calculations.

If the temperature and ionic medium are kept constant, the solubility of Ag(I) is a function of the halide concentration $[A]$ only ($A = \text{Cl, Br}$). With increasing $[A]$, the solubility first decreases, but then passes through a minimum and finally increases again at an increasingly rapid rate, due to the formation of soluble complexes between Ag^+ and the halide ions.¹¹⁻¹³

In the present case, a silver halide precipitate is in contact with a solution of an initial halide concentration C_A and a Tl(III) concentration C_M . The solubility l is measured. The total halide concentration at equilibrium, $C_A + l$, is thus known. This quantity is present, partly as free halide ions, partly as complexes of Ag(I) (ligand number \bar{n}_S) or Tl(III) . Hence, provided that only mononuclear complexes exist:

$$C_A + l = [A] + l\bar{n}_S + C_M\bar{n}_M \quad (2)$$

In the special case when no Tl(III) is present, $C_M = 0$

$$[A] = C_A - l(\bar{n}_S - 1) \quad (3)$$

Here, $l(\bar{n}_s - 1)$ is only a small correction term except for very small C_A , where on the other hand the correction is easily determined, as $\bar{n}_s \simeq 0$, and therefore

$$[A] = C_A + l \quad (4)$$

For higher C_A , the quantity $\bar{n}_s - 1$ is obtained¹¹ as the slope of a curve $\log l$ versus $\log [A]$.

It is thus possible to determine the connexion between l and $[A]$ by measurements in solutions free from Tl(III). Once this connexion is known, $[A]$ can be found for a solution containing Tl(III) as well, only by determination of the solubility of Ag(I). Then it is possible to calculate \bar{n}_M from eqn. (2), the correction term $l(\bar{n}_s - 1)$ being determined as described above.

Experimental

Chemicals. Thallium(III) perchlorate and sodium perchlorate were prepared and analysed as before.¹ All other chemicals were of analytical grade and used without further purification.

To make measurements possible even at very low chloride concentrations, it was necessary to determine the chloride present as an impurity in the medium used. All perchlorates were prepared from the same batch of perchloric acid ("Baker Analysed"), the chloride concentration of which was $\leq 0.0005\%$, according to the manufacturer. This means a chloride concentration of about 2×10^{-5} M in a 4 M solution. Such a concentration can hardly be determined by direct silver titration so the following method was applied:

From a solution with $[\text{Cl}^-] \approx 1 \times 10^{-5}$ M, $[\text{ClO}_4^-] = 4$ M, portions of v ml ($v = 5, 10, 20$) were carefully diluted to 100 ml with a solution of HClO_4 and NaClO_4 , $[\text{ClO}_4^-] = 4$ M. These solutions were titrated potentiometrically with 0.01 M silver nitrate solution added from an Agla micrometer syringe. The chloride concentrations so determined were on a straight line when plotted against v . Extrapolation to $v = 0$ gives the chloride concentration in the original perchlorate solution. The value found was 1.8×10^{-5} M.

Radioactive silver halides were prepared in the following way. A precisely weighed piece of an irradiated silver plate, containing ^{110m}Ag ($t_{1/2} = 253$ d) was dissolved in a small portion of nitric acid. In order to minimize the risk of a radiation induced reduction of the silver halide, a certain amount of inactive silver nitrate solution was added, *viz.* about 50 % of the total amount in the case of chloride, and 85 % in the case of bromide. The activity was then about 0.2 and 0.07 mC/mmmole for chloride and bromide, respectively. From the hot nitrate solutions, the halides were precipitated, and then washed several times with hot dilute HClO_4 . The chloride was allowed to age for several days, the bromide for 20 h in contact with the final wash solutions, kept at 80°C. The precipitates were then transferred to the column and the solubility runs started without delay. During all these operations the silver halides were protected from light.

Radioactivity measurements. The activity was measured with a γ -scintillation counter. With samples of 5 ml, the geometry factor was about 16 %, giving for the silver chloride solutions a counting rate of 400×10^6 cpm M^{-1} , for the silver bromide solutions 120×10^6 cpm M^{-1} . In the case of very low solubilities, samples of 10 ml were analysed, with the geometry factor 20 %, rendering the counting rates 1000×10^6 and 300×10^6 cpm M^{-1} , respectively. The counter was calibrated by means of suitably diluted samples of the used active silver nitrate solutions.

As the background was of the magnitude 500 cpm, only solubilities higher than 0.5×10^{-6} M (chloride) or 2×10^{-6} M (bromide) could be measured with the desired accuracy.

The solubility column. The silver halide was held in a glass tube, the length of which was 80 mm and the internal diameter 4 mm, by a sintered glass disc of porosity 4. Under this disc, the glass tube was bent upwards and fitted with a stop-cock, then bent downwards again, ending with a tip. The upper end of the column had been widened to a funnel which was connected with two partially water filled communicating vessels. The

difference in height between these vessels could be altered so as to give any suitable air pressure over the column. The connexion between the funnel and the pressure vessels could easily be broken in order to introduce additional amounts of solution into the column.

About 0.35 g of halide was used (2.5 mmole AgCl, 2.1 mmole AgBr), resulting in a bed about 3 cm high.

The volume of the column from the bottom of the funnel to the tip was about 4 ml. For a complete displacement of a solution standing in the column, 12–15 ml of the next solution to be measured had to pass. This portion was then discarded.

Under a pressure of 50 cm water, the flow through the column was about 30 ml h⁻¹ (250 ml h⁻¹ cm⁻²). The main flow resistance was due to the sintered glass disc.

The column was surrounded by a lead cylinder with 30 mm thick walls and immersed in a thermostated water bath. The lead and the water served as a radiation shield.

The silver halides were protected from light with black tape, wound round the column. The white colour of the halides was still preserved when the measurements were finished.

Equilibration. Chloride solutions passing through silver chloride reached equilibrium after one single run through the column, except for solutions of very low C_A . Bromide solutions in contact with silver bromide did not arrive at equilibrium so readily; they had to pass the column two or three times. Each solution was cycled until the measured activity stayed constant (Table 2).

In the very first measurements with a precipitate not used before, the equilibrium was approached from higher activities, which certainly is contrary to expectation. The apparent explanation is that very small solid particles first passed the glass filter but that the filter soon became tightened, so as to hold the particles when the solution was run through a second time.

Table 2. Equilibration: Apparent solubility after repeated passage of a solution through the column. (Powers of ten not specified.)

Run →			1	2	3	4	5
Ligand	C_M M	C_A M	$l \times 10^n$ M				
Cl ⁻	0	6.9×10^{-5}	3.6	3.8	4.0	4.1	4.1
	„	0.100	2.33	2.31			
	„	0.400	1.62	1.61			
	„	0.700	4.49	4.52			
	„	1.600	2.29	2.30			
Br ⁻	0.005	0.007	3.78	3.78			
	0	0.400	5.14	5.32	5.32		
„	0.500		8.35	9.00	9.02		

Table 3. Reproducibility: Solubility obtained by equilibrating solutions (A and B) of the same composition. (Powers of ten not specified.)

Ligand	C_M M	C_A M	$l \times 10^n$ M	
			A	B
Cl ⁻	0	0.200	5.28	5.31
	„	0.700	4.49	4.49
	„	1.600	2.30	2.30
	0.005	0.007	3.78	3.84

Reproducibility. Several measurements were checked by equilibrating a new solution of the same composition. A few examples are listed in Table 3. The reproducibility is good.

Results

The chloride system. When $C_M = 0$, C_A was mostly chosen between 0.030 and 2.0 M. To make possible a comparison with previous work¹ in a region of $[A]$ where the complex formation of Tl(III) is not yet completed, a few measurements were also performed with C_A between 1.8×10^{-5} and 11.9×10^{-5} M. The lower limit $C_A = 1.8 \times 10^{-5}$ was set by the chloride content of the perchloric acid making up the medium. In the intermediate range, from $C_A \approx 10^{-4}$ up to $C_A \approx 0.030$ M, the solubility is too low to be measured under the present conditions.

The observed solubilities, l_{obs} , are in Table 4, together with the values of $[A]$ calculated from eqn. (3), and the solubilities l_{calc} , obtained from the constants finally calculated (see note below). In Fig. 3, $\log l_{\text{obs}}$ is plotted against

Table 4. The solubility l_{obs} as a function of $[A]$ for the silver chloride and bromide systems ($C_M = 0$). The solubility l_{calc} from the best set of stability constants.

C_A M	l_{obs} M	$[A]$ M	l_{calc} M	C_A M	l_{obs} M	$[A]$ M	l_{calc} M
Chloride				Bromide			
1.8×10^{-5}	2.0×10^{-6}	2.0×10^{-5}	2.0×10^{-6}	0.100	3.67×10^{-6}	= C_A	3.6×10^{-6}
6.9×10^{-5}	6.5×10^{-7}	7.0×10^{-5}	6.5×10^{-7}	0.140	6.70×10^{-6}	»	6.6×10^{-6}
11.9×10^{-5}	4.1×10^{-7}	11.9×10^{-5}	4.2×10^{-7}	0.200	1.214×10^{-5}	»	1.27×10^{-5}
0.030	6.88×10^{-7}	= C_A	6.9×10^{-7}	0.300	2.89×10^{-5}	»	2.9×10^{-5}
0.100	2.32×10^{-6}	»	2.3×10^{-6}	0.400	5.32×10^{-5}	»	5.4×10^{-5}
0.140	3.35×10^{-6}	»	3.5×10^{-6}	0.500	9.02×10^{-5}	»	8.8×10^{-5}
0.200	5.30×10^{-6}	»	5.5×10^{-6}	0.700	1.898×10^{-4}	»	1.93×10^{-4}
0.300	9.94×10^{-6}	»	10.0×10^{-6}	1.000	4.66×10^{-4}	0.999	4.5×10^{-4}
0.400	1.61×10^{-5}	»	1.60×10^{-5}	1.280	8.37×10^{-4}	1.278	8.4×10^{-4}
0.500	2.37×10^{-5}	»	2.4×10^{-5}	1.600	1.510×10^{-3}	1.596	1.49×10^{-3}
0.700	4.50×10^{-5}	»	4.5×10^{-5}	2.000	2.695×10^{-3}	1.993	2.7×10^{-3}
1.000	8.76×10^{-5}	»	9.6×10^{-5}				
1.280	1.479×10^{-4}	»	1.69×10^{-4}				
1.600	2.296×10^{-4}	»	2.9×10^{-4}				
2.000	3.795×10^{-4}	1.999	5.1×10^{-4}				

$\log [A]$ in the region $0.030 \leq [A] \leq 2.0$. A smooth curve is drawn through the points. This curve describes l as a function of $[A]$ under the present conditions and is therefore used as calibration curve for the following measurements.

In the region of low $[A]$ ($\leq 10^{-4}$), corresponding values of l and $[A]$ are obtained in another way, *viz.* by the function¹¹ (K_s denotes the solubility product of AgCl)

$$l = \frac{K_s}{[A]} + [AgA] \quad (5)$$

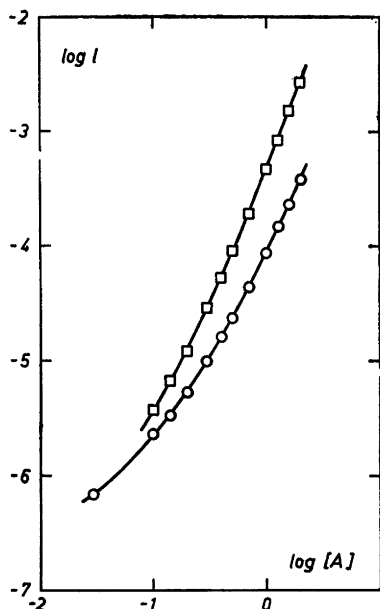


Fig. 3. Solubility curves of the silver chloride (O) and bromide (□) systems at high values of [A].

higher complexes being negligible for these [values] of [A]. With $K_s = 0.38 \times 10^{-10} \text{ M}^2$ and $[\text{AgA}] = 1.1 \times 10^{-7} \text{ M}$, eqn. (5) describes the connexion between l and [A] experimentally obtained when $C_M = 0$, Table 4. As eqn. (5) is valid for all values of $[\text{A}] \leq 10^{-4}$, it is possible to find [A] for a solution, also containing Tl(III), even if its value of [A] is much lower than those measured when the constants K_s and $[\text{AgA}]$ are determined. A lower limit is set only as the solubility becomes inconveniently high.

A series of solutions with $C_M = 5.02 \times 10^{-3}$ and C_A between 5×10^{-3} and $10 \times 10^{-3} \text{ M}$ was then measured. In these solutions, \bar{n}_M is far from its final value of N . From the obtained values of l , [A] is calculated by eqn. (5), Table 5. Values of \bar{n}_M are calculated by eqn. (2). Fig. 6 shows that these values agree very well with those obtained from the Tl(III)/Tl(I) measurements.

In the region of high chloride concentration, a value of C_M as high as possible was desirable in order to obtain reliable values of \bar{n}_M even at very high chloride concentration (*cf.* eqn. (2)). To check whether the presence of thallium(III) affected the medium and so caused a change in the solubility, two values of C_M were chosen, *viz.* 25.3×10^{-3} and $50.6 \times 10^{-3} \text{ M}$. The measured solubilities and the values of [A] and \bar{n}_M , hence obtained, are in Table 5. In Fig. 6, \bar{n}_M is plotted against $\log [\text{A}]$. No difference appears between the two series of different C_M . Within the limits of error, $\bar{n}_M = 4$ in the wide range of [A] studied.

The bromide system. The solubility product and the minimum solubility of silver bromide are considerably lower than those of silver chloride.^{11,13} Therefore it was not possible to measure solubilities at bromide concentrations $< 0.1 \text{ M}$.

Table 5. The thallium(III) chloride system: Determination of \bar{n}_M as a function of [A] by solubility measurements.

$C_M \times 10^3$ M	C_A M	l M	[A] M	\bar{n}_M
5.06	5.02×10^{-3}	1.76×10^{-4}	2.16×10^{-7}	1.03
	7.02×10^{-3}	3.80×10^{-5}	1.00×10^{-6}	1.39
	9.52×10^{-3}	4.25×10^{-6}	9.1×10^{-6}	1.88
25.3	0.160	1.29×10^{-6}	0.059	4.0
	0.200	2.31×10^{-6}	0.100	4.0
	0.320	6.24×10^{-6}	0.222	3.9
	0.400	1.005×10^{-5}	0.301	3.9
	0.640	2.75×10^{-5}	0.541	3.9
	0.800	4.55×10^{-5}	0.704	3.8
50.6	0.300	2.26×10^{-6}	0.099	4.0
	0.900	4.56×10^{-5}	0.705	3.9
	1.200	9.07×10^{-5}	1.000	4.0
	1.600	1.80×10^{-4}	1.410	3.8
	2.200	3.81×10^{-4}	2.005	3.9

Table 6. The thallium(III) bromide system: Determination of \bar{n}_M as a function of [A] by solubility measurements. $C_M = 48.8 \times 10^{-3}$ M.

C_A M	l M	[A] M	\bar{n}_M
0.300	4.00×10^{-6}	0.105	4.0
0.400	1.35×10^{-5}	0.205	4.0
0.600	5.48×10^{-5}	0.406	4.0
0.900	1.984×10^{-4}	0.705	4.0
1.198	4.60×10^{-4}	1.002	4.0
1.597	1.035×10^{-3}	1.392	4.1
2.190	2.688×10^{-3}	1.992	3.9

The connexion between l and [A] for the bromide in the range $0.1 \leq C_A \leq 2.0$ M is given in Table 4 and Fig. 3. As the curve l as a function of [A] is even more steep than in the case of chloride, it is a still more sensitive instrument for the determination of [A].

The values of \bar{n}_M , obtained from measurements of the solubilities in solutions with $C_M = 48.8 \times 10^{-3}$ M, Table 6, show no tendency to reach values higher than 4.

Note on the complex formation of silver with the halides. From the solubility data it is possible to derive the constants $^{11}K_s \beta_n$, $n = 2, 3, 4$, for both silver halide systems. For the chloride system, the solubility product K_s and the constant $K_s \cdot \beta_1$ are also computable and hence the stability constants β_n , $n = 1, 2, 3, 4$.

For the chloride system, the experimental data are best fitted by the following set of constants: $K_s = 0.4 \times 10^{-10}$ M², $\beta_1 = 2.8 \times 10^3$ M⁻¹, $\beta_2 = 4.7 \times 10^5$ M⁻², $\beta_3 = 1.0 \times 10^6$ M⁻³, $\beta_4 = 1.1 \times 10^6$ M⁻⁴.

In Table 4, the solubilities calculated from these constants are given (l_{calc}). They agree with the measured solubilities except for the highest chloride concentrations ($[A] > 0.7 \text{ M}$) where $l_{\text{obs}} < l_{\text{calc}}$. This is probably due to the medium change caused by the exchange of perchlorate ions for chloride ions (*cf.* p. 2138).

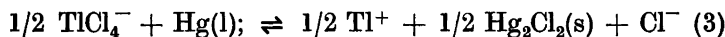
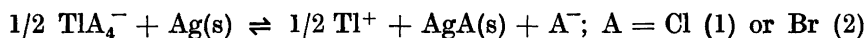
For the bromide system, the experimental solubility curve is best fitted by the constants $K_s\beta_3 = 1.25 \times 10^{-5}$, $K_s\beta_2 = 2.15 \times 10^{-4} \text{ M}^{-1}$ and $K_s\beta_4 = 2.25 \times 10^{-4} \text{ M}^{-2}$, the first complex being negligible within the region studied here. The values of l_{obs} and l_{calc} , Table 4, agree within the limits of error.

Bearing in mind the difference in temperature and medium, the constants found agree well with Leden's values^{11,13} for both systems.

EMF MEASUREMENTS

The free halide concentration of a solution can often be determined by second order electrodes, *e.g.* Ag/AgCl or Hg/Hg₂Cl₂ electrodes. In solutions containing Tl(III), however, the high redox potential renders the use of such electrodes dubious.

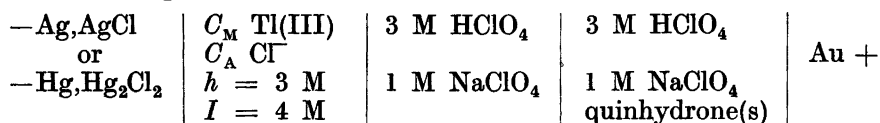
Assuming the pertinent standard potentials¹⁴ to have approximately the following values in the present medium: Tl⁺/Tl³⁺, 1.25 V; Ag/Ag⁺, 0.80 V; Hg/Hg₂²⁺, 0.79 V; it is obvious that metallic silver and mercury should be oxidised when no halide is present. In solutions containing an excess of halide, the oxidations will take place according to the following reactions



With the stability constants¹ β_4 for TlCl₄⁻ $4 \times 10^{19} \text{ M}^{-4}$, for TlBr₄⁻ $5 \times 10^{26} \text{ M}^{-4}$ and the solubility products K_s for AgCl $0.4 \times 10^{-10} \text{ M}^2$ (*cf.* above), for AgBr¹³ $2 \times 10^{-13} \text{ M}^2$ and for Hg₂Cl₂¹⁴ $1 \times 10^{-18} \text{ M}^3$, the following values are calculated for the equilibrium constants of the reactions (1), (2) and (3): $K_1 = 10^8$, $K_2 = 10^7$, $K_3 = 10^7 \text{ M}$. Consequently, oxidation may occur also in halide solutions. To see whether it really does, an investigation of the performance of the silver chloride and calomel electrodes was undertaken.

C a l c u l a t i o n s

The following cell was studied:



For the emf E we have

$$E = e_{\text{RE}} - e^\circ + \frac{RT}{F} \ln (f_A[A]) - e_d \quad (6)$$

The reference electrode potential e_{RE} , the liquid junction potential e_d , the standard potentials e° and the activity factor f_A may be considered as constants and thus joined into a constant term E° :

$$E = E^\circ + \frac{RT}{F} \ln [A] \quad (7)$$

When no Tl(III) is present, $C_M = 0$, eqn. (3) can be used to calculate $[A]$, and as $l \ll C_A$ in the range measured, the approximation $[A]_s = C_A$ is valid. If, in this special case, E is denoted E' , eqn. (7) takes the form

$$E' = E^\circ + \frac{RT}{F} \ln C_A \quad (8)$$

By eqn. (8), E° is calculated from corresponding \bar{n}_M values of E' and C_A . The value of E° thus being known, $[A]$ can be found for solutions containing Tl(III) from the measured values of E (eqn. (7)).

In the case of the Ag/AgCl electrodes, the corresponding ligand numbers \bar{n}_M are then calculated from eqn. (2), where in practice various terms can be neglected, dependent upon the actual value of $[A]$. For the extremely low values of $[A]$ prevailing when $C_A < C_M$, $[A]$ is much lower than C_A and, moreover, the formation of silver complexes is negligible, $\bar{n}_S = 0$. On the other hand $[Ag^+]$ can be fairly high before K_S for $AgA(s)$ is reached and therefore l cannot be neglected in comparison with C_A . Hence

$$\bar{n}_M = (C_A + l)/C_M \quad (9)$$

where the solubility l is obtained from the solubility measurements (eqn. (5)). For higher values of $[A]$, l soon becomes $\ll C_A$, whereas finally $[A]$ cannot be neglected in comparison with C_A . Then it is valid

$$\bar{n}_M = (C_A - [A])/C_M \quad (10)$$

For high values of $[A]$, the calculation is thus independent of the solubility measurements.

The case of the Hg/Hg₂Cl₂ electrode needs no consideration, as these measurements were unsuccessful (p. 2137).

Experimental

Silver chloride electrodes were prepared according to Brown.¹⁵ They were formed as a disc of ≈ 0.8 cm² area, suspended by a wire.

Calomel electrodes, responding to variations in the chloride concentration, were prepared according to Hills and Ives,¹⁶ as follows. A suitable electrode vessel was made water repellent with silicone oil. Some pure mercury (Merck) was poured into the vessel. A few ml of mercury were shaken in a stoppered bottle with a little calomel ("Baker Analysed", dried and ground before use) until the mercury was covered with a grey, pearly "skin" of calomel. Part of this skin was transferred to the mercury in the electrode vessel where it spread over its whole surface. A platinum wire sealed into a glass tube was immersed in the mercury and the electrode solution was introduced.

Reference electrodes. A quinhydrone electrode of the type described earlier¹ was used.

Procedure. The halide half-cells contained known volumes of a solution S, with C_M M thallium(III) perchlorate (C_M sometimes = 0), 3 M perchloric acid and sodium perchlorate to make $I = 4$ M. The quinhydrone reference electrode was connected. From a burette, portions were added of a solution T of the same C_M , h and I as S, but in addition also containing a certain concentration of hydrochloric acid. In order to exclude oxygen

and provide a rapid mixing, a stream of pure nitrogen was passed through the solution, both before the titration and upon each addition of the solution T. The emf was measured after each addition.

Two electrodes of each kind were used in the silver chloride measurements, one calomel and two reference electrodes in the calomel series. The different combinations generally agreed within 0.1 mV. When a titration series was repeated the reproducibility was within 0.3 mV, when $C_M = 0$, and within 0.5 mV, with few exceptions, when $C_M \neq 0$.

R e s u l t s

The silver chloride electrode. The result of the determination of E° is found in Table 7 and Fig. 4. The values show a slight decrease with [A]. On extrapolation to $[A] = 0$, $E^\circ = 531.5$ mV is obtained.

To find the right value of [A] in the following measurements, involving Tl(III), $E^\circ = 531.5$ mV was used in eqn. (7) as a first approximation. From the value of [A] thus found, a better value of E° was obtained from Fig. 4. This procedure was repeated until [A] stayed constant.

With solutions containing Tl(III), two series of titrations were performed, with $C_M = 8.00 \times 10^{-3}$ and 25.0×10^{-3} M. Table 8 contains the measured values of E and the values of [A] and \bar{n}_M calculated from these. In Fig. 6, \bar{n}_M is plotted against $\log [A]$, to be compared with values obtained by other methods.

The following features emerge: (1) When the chloride concentration is low, $[A] < 10^{-2}$, the agreement between the Ag/AgCl and the Tl(III)/Tl(I) measurements is excellent. (2) At higher values of [A] the results of the two methods differ appreciably, the silver chloride electrode rendering much lower values of [A], and consequently much higher values of \bar{n}_M . That those values are wrong is shown by the fact that \bar{n}_M does neither stop at 4, nor at 6 or at any other reasonable value. Furthermore, the two series of different C_M

Table 7. Determination of E° for the Ag/AgCl cell.

C_A M	E' mV	E° mV
3.23×10^{-3}	386.7	531.6
12.43×10^{-3}	420.5	531.3
18.07×10^{-3}	430.1	531.5
0.0284	441.7	531.6
0.0321	444.7	531.5
0.0500	455.8	531.5
0.0642	461.9	531.2
0.0800	467.6	531.4
0.1244	478.2	530.9
0.1250	478.7	531.2
0.1805	487.4	530.6
0.284	498.6	530.2
0.500	511.9	529.4
0.800	522.6	528.2
1.250	531.9	526.3

do not coincide in the region of high [A], the deviation from the Tl(III)/Tl(I) measurements being larger, the higher the value of C_M .

The obtained emf values were fairly reproducible for all [A] except in a region around $[A] = 10^{-2}$, where a small continuous drift was observed. Electrodes once used at high chloride concentrations gave in most cases the same result as before, when used again at low concentrations. However, the electrodes had a marked tendency to deteriorate. Used in a couple of titrations they suddenly showed an abnormal behaviour, the colour of the silver chloride then being paler than that of a fresh electrode.

To sum up, the emf measurements indicate that the oxidation of silver by thallium(III) is strongly inhibited in solutions of low chloride concentrations. The inhibition is decreased, however, when the chloride concentration grows larger ($[Cl^-] < 10^{-2}$, if $C_M \approx 10^{-2}$), with the breakdown of the electrode function as a consequence.

The calomel electrode. The result from the titration in thallium-free solution is presented in Fig. 5, yielding a value of $E^\circ = 487.7$ mV when $[A] = 0$. Titrations with thallium present were not successful. The introduction of a solutions S, containing Tl(III) but no chloride, did not visibly change the electrode, but the further addition of a small amount of chloride immediately destroyed the calomel "skin" with the result that no relevant emf values were obtained.

Mercury thus seems to be rapidly oxidized by thallium(III) even in solutions of very low chloride concentrations; no inhibition is observed in this case.

Table 8. The thallium(III) chloride system: Determination of \bar{n}_M as a function of [A] by the Ag/AgCl electrode.

$C_A \times 10^3$ M	E mV	[A] M	\bar{n}_M	$C_A \times 10^3$ M	E mV	[A] M	\bar{n}_M
$C_M = 8.00 \times 10^{-3}$ M							
1.66	86.4	2.2×10^{-8}	0.42	90.9	455.6	5.01×10^{-2}	5.10
3.23	94.7	3.1×10^{-8}	0.56	143.0	470.8	9.27×10^{-2}	6.29
6.27	119.3	8.2×10^{-8}	0.84	200	481.2	0.140	7.50
9.11	156.6	3.6×10^{-7}	1.15	400	500.9	0.315	10.6
11.78	189.1	1.30×10^{-6}	1.48	625	512.3	0.511	14.3
14.30	223.8	5.2×10^{-6}	1.79	$C_M = 25.0 \times 10^{-3}$ M			
15.49	251.5	1.54×10^{-5}	1.94	16.4	103.3	4.4×10^{-8}	0.69
16.39	273.2	3.6×10^{-5}	2.05	32.1	171.0	6.4×10^{-7}	1.29
16.67	281.0	4.9×10^{-5}	2.08	47.6	241.3	1.03×10^{-5}	1.90
20.0	323.0	2.6×10^{-4}	2.47	62.5	322.1	2.52×10^{-4}	2.49
25.0	356.4	9.8×10^{-4}	3.00	77.0	355.9	9.6×10^{-4}	3.04
29.4	378.9	2.4×10^{-3}	3.38	90.9	384.1	2.94×10^{-3}	3.52
32.1	390.1	3.7×10^{-3}	3.55	104.6	406.6	7.2×10^{-3}	3.90
33.3	394.2	4.4×10^{-3}	3.61	117.7	420.2	1.23×10^{-2}	4.22
40.0	411.9	8.8×10^{-3}	3.90	143.0	436.1	2.30×10^{-2}	4.80
47.6	423.1	1.37×10^{-2}	4.24	200	457.6	5.4×10^{-2}	5.83
50.0	427.5	1.63×10^{-2}	4.20	400	484.7	0.161	9.56
62.5	439.4	2.63×10^{-2}	4.53	625	497.6	0.274	14.0
75.0	447.0	3.53×10^{-2}	4.95				

Direct proof of the oxidation of silver and mercury by thallium(III). If silver, as powder, is shaken with a chloride solution of Tl(III), the formation of AgCl(s) is soon observed. The rate of reaction increases with the chloride concentration, being quite low at low concentrations. In chloride-free solution, both silver and mercury are fairly rapidly oxidized (cf. the effect of halide on the rate of the Tl(III)/Tl(I) electron exchange^{7,17-19}).

DISCUSSION

The opinion expressed above (p. 2134) that the exchange of perchlorate for chloride ions causes an appreciable change of the medium, is supported by other facts. Thus the shift in E° (Figs. 4 and 5) can only be explained on this

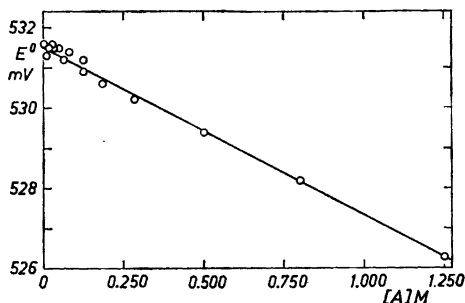


Fig. 4. The connexion between E° and $[A]$ for the Ag/AgCl cell.

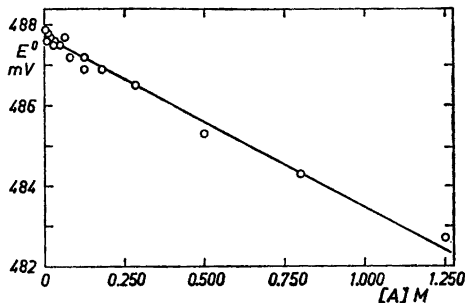


Fig. 5. The connexion between E° and $[A]$ for the Hg/Hg₂Cl₂ cell.

basis. It is significant that the slopes of the two lines are exactly the same. This variation of E° is furthermore equivalent to the variation of the solubility product of AgCl, as determined by Leden.¹²

For low concentrations of chloride ions, $[A] < 10^{-2}$ M, the complex formation curve found from the Ag/AgCl, as well as from the solubility measurements, agrees very well with that obtained by the Tl(III)/Tl(I) method, Fig. 6. The values of the stability constants β_1 to β_3 , reported before¹ for the chloride system, are thus fully corroborated. An analogous check for the bromide system would no doubt yield the same result.

For high concentrations of chloride or bromide ions, the solubility measurements confirm beyond doubt the conclusion drawn from emf work with the Tl³⁺/Tl⁺ electrode^{1,9} that at most four Cl⁻ or Br⁻ can be coordinated around Tl³⁺ in aqueous solution, at least for $[A] \leq 2$ M (Fig. 6). It should be stressed that no other interpretation is possible. This result of course lends further support to the opinion that the silver halide electrodes fail for high chloride concentrations.

The check of the Ag/AgCl electrode in the presence of thallium(III) thus shows on the one hand that reasonable values can be found for the stability constants β_1 to β_3 of the thallium(III) chloride and bromide systems by the use of silver halide electrodes but on the other hand, and more important,

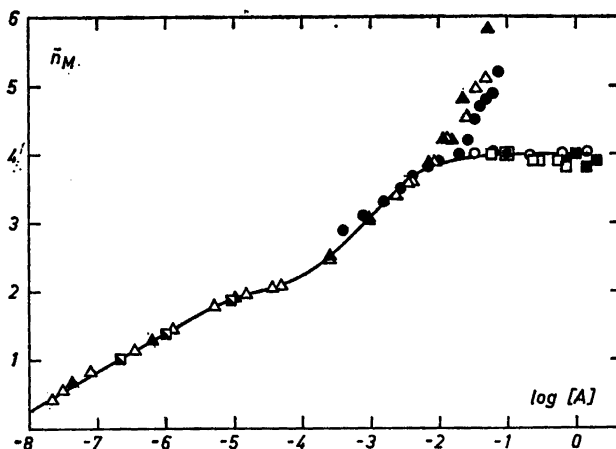


Fig. 6. The complex formation function of the thallium(III) chloride system, as obtained by various methods of measurement and calculation. The central ion measurements, by the Tl(III)/Tl(I) electrode, have yielded: 1) Full-drawn curve, calculated from the constants β_1 to β_4 ; 2) Filled circles, from the slopes and intercepts of the C_A , C_M -lines¹ at constant E_{MP} ; 3) Open circles, from the slope of the function E_{MP} ($\log A$), according to the Bodländer equation (Table 1). The ligand ion measurements, by the Ag/AgCl electrode, have yielded (Table 8): 4) Filled triangles, when $C_M = 25$ mM; 5) Open triangles, when $C_M = 8$ mM. The solubility measurements have yielded (Table 5): 6) Filled squares, when $C_M = 50$ mM; 7) Open squares, when $C_M = 25$ mM (both at high values of $[A]$); 8) Half-filled squares, when $C_M = 5$ mM (at low values of $[A]$). For the sake of clarity, only a representative choice of points have been plotted from Table 1.

that completely erroneous results are obtained at higher halide concentrations, due to the manifest failure of the electrodes under these conditions.

A maximum coordination number of four is also arrived at by Leden and Ryhl,³ from studies of the thermodynamic properties of the thallium(III) chloride and bromide complexes, performed in the same medium as used in this work. They find that no more heat is evolved on further addition of ligand, when $C_A > 4C_M$. The only reasonable explanation is that the complex formation is complete with TlA_4 . Also the extraction experiments of Dodson²⁰ and of Nord and Ulstrup²¹ lead to the same conclusion.

The data of Leden and Ryhl³ also permit a recalculation of our constants to the temperature of 25°C (Table 9). For the chloride system, a direct comparison is then possible with the constants reported for 25°C by other recent investigators, Table 10. With due consideration to the different media used, the values are on the whole fairly consistent. One obvious discrepancy still exists, however, *viz.* the poor agreement between the values of K_4 at $I = 0.5$ M, obtained by various methods,^{9,20} or even by the same method.^{20,21}

Table 9. Stability constants for the thallium(III) chloride and bromide systems, recalculated to 25°C.

		Cl ⁻	Br ⁻
β_1	M ⁻¹	$(3.0 \pm 0.3) \times 10^7$	$(3.2 \pm 0.1) \times 10^9$
β_2	M ⁻²	$(1.8 \pm 0.2) \times 10^{13}$	$(7.5 \pm 0.5) \times 10^{16}$
β_3	M ⁻³	$(4.5 \pm 0.5) \times 10^{16}$	$(2.0 \pm 0.3) \times 10^{22}$
β_4	M ⁻⁴	$(2.8 \pm 0.4) \times 10^{19}$	$(2.7 \pm 0.2) \times 10^{26}$

Table 10. Some recent determinations of the stability constants of the thallium(III) chloride system at 25°C.

Authors	Methods	$\frac{I}{M}$	log K_n			
			1	2	3	4
	$n \longrightarrow$					
This work	Tl ³⁺ /Tl ⁺ ; Ag/AgCl; solubility	4.0	7.48	5.78	3.39	2.80
King <i>et al.</i> ⁹	Tl ³⁺ /Tl ⁺ ; sol. {	3.0	7.16	5.44	3.55	2.17
		0.5	6.72	5.10	2.68	1.81
	estimated \longrightarrow	0	7.72	5.76	3.00	1.81
Dodson ²⁰	extr. { ipe * TBP **	0.5	—	—	2.70	1.61
			—	—	2.68	1.61
Nord and Ulstrup ²¹	extr. ipe	0.5	—	—	—	1.38
		0	—	—	3.03	1.47

* = isopropyl ether

** = tributyl phosphate

Professor Ido Leden has strongly promoted this work by his valuable comments and fruitful proposals.

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