72. *Formation Constants of* $HgBr_3^-$ *and* $HgBr_4^{2-}$ *at* 5°, 25°, *and* 35° *in Aqueous Medium of Constant Ionic Strength and Acidity.*

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The formation constants of the ions $HgBr_3^-$ and $HgBr_4^{2-}$ have been measured at 5°, 25°, and 35° over a wide range of free bromide concentrations by a new method in which bromine and mercuric bromide compete for bromide ions. The results at 25° have been confirmed at low free bromide-ion concentrations through the absorption spectra of the solutions containing the complex ions. The constants obtained at this temperature differ slightly from the earlier values obtained over a limited and rather high range of free bromide-ion concentrations. Evidence for the formation of a weak donor–acceptor complex $HgBr_6^{2-}$ from $HgBr_4^{2-}$ and Br_2 has been obtained. The thermodynamic constants for the formation of $HgBr_3^-$ and of $HgBr_4^{2-}$ have been estimated from the measured formation constants.

AQUEOUS solutions of the sparingly soluble mercuric halides contain principally the undissociated HgX_2 molecules ($X = Cl, Br, I$), a small proportion of HgX^+, and negligible amounts of Hg^{2+}. In the presence of excess of halogen ions, the solubility of the mercuric halide is greatly increased; it is generally agreed that this enhanced solubility is due to the formation of the complex anions HgX_3^- and HgX_4^{2-}. Thus the species HgX^+, HgX_2, HgX_3^-, HgX_4^{2-} form a set of successive co-ordination complexes of Hg^{2+} with X^- as the co-ordinating group. The equilibria involved in the formation of these complexes have frequently been studied, most recently by Sillén and his associates[1-8]; the addition of the first two halogen anions to the mercuric ion takes place with great ease, the complexes HgX^+ and HgX_2 being very stable. On the other hand, the higher complexes HgX_3^-, HgX_4^{2-} are much less stable, and this might suggest that two of the ligand groups in HgX_4^{2-} are held more firmly than the rest. However, the most recent evidence, from Raman spectra,[9,10] suggests that all four bonds in HgX_4^{2-} are equivalent, and that the ion is tetrahedral. A pyramidal configuration has been suggested [9] for the ion HgX_3^-, though it is equally possible to interpret the spectroscopic evidence in terms of a tetrahedral configuration, the vacant co-ordination position being occupied by a water molecule.[10] In any event, the addition of further X^- ions to HgX_2 involves, according to this evidence, a fundamental change in structure.

The only modern study of the equilibrium constants of the mercuric bromide–bromide ion system, by Bethge, Jonevall-Westöö, and Sillén,[6] was limited to one temperature (25°) and to rather high free bromide-ion concentrations, and the constants were obtained indirectly by combining the results of several electrometric titrations. A direct electrometric determination of the free bromide-ion concentration does not seem to be easy, and the method developed in the preceding paper of using bromine as indicator has been used here. The ionic strength and acidity ($I = 0{\cdot}5$; pH $= 2$) of the solutions were maintained constant at approximately † the values used by Sillén *et al.*[1-8] by adding sodium perchlorate and perchloric acid, and experiments were carried out at 5°, 25°, and 35°. At low free bromide-ion concentrations the observations at 25° were supplemented by a study of the light absorption at λ 310 mμ.

The great difference in stability between HgX_2 and the anions HgX_3^- and HgX_4^{2-} makes it possible to study their formation constants as if HgX_2 were the central group, *i.e.*, the ionisation of HgX_2 can be neglected in the presence of even small amounts of free X^-. In the following discussion therefore it is assumed that only the following equilibria need be considered:

$$HgBr_2 + Br^- \rightleftharpoons HgBr_3^- : K_{2,3} \equiv [HgBr_3^-]/[HgBr_2][Br^-]$$
$$HgBr_3^- + Br^- \rightleftharpoons HgBr_4^{2-} : K_{3,4} \equiv [HgBr_4^{2-}]/[HgBr_3^-][Br^-]$$

The earlier workers used χ_3 instead of $K_{2,3}$ and χ_4 for the product $K_{2,3}\,.\,K_{3,4}$; the present notation has been adopted to provide a logical set applicable to each successive stage in the complex formation.

EXPERIMENTAL

(i) *Bromine Indicator Method.*—The procedure was that described in the preceding paper for the bromine–bromide ion system except that a known quantity of pure mercuric bromide was added to the solution containing the sodium bromide. Hydrolysis corrections were made to all measured values of $[Br_2^F]$* by use of the correction terms used for the bromine–bromide ion system at the appropriate temperature. There is a slight additional complication in the calculation since the total combined bromide ($[^TBr_C^-]$) is now made up of the bromide combined with the mercuric bromide ($[^mBr_C^-] = C_L - [L]$ where [L] represents the free ligand concentration, and C_L is the total concentration of ligand available for combination with the mercuric bromide present) and that combined with the bromine ($[^bBr_C^-]$). Eqns. (1)—(3), in the notation

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† In the bromine indicator method it was convenient to use a molal rather than a molar scale of concentration, and both ionic strengths and acidities have been calculated on this basis. The conditions used were not therefore quite the same as those used by Sillén *et al.*

[1] Sillén, *Svensk kem. Tidskr.*, 1946, **58**, 52.
[2] Sillén and Infelt, *ibid.*, p. 61.
[3] Jonsson, Qvarfort, and Sillén, *Acta Chem. Scand.*, 1947, **1**, 461.
[4] Sillén, *ibid.*, p. 473.
[5] Lindgren, Jonsson, and Sillén, *ibid.*, 1948, **1**, 479.
[6] Bethge, Jonevall-Westöö, and Sillén, *ibid.*, 1948, **2**, 828.
[7] Qvarfort and Sillén, *ibid.*, 1949, **3**, 505.
[8] Sillén, *ibid.*, p. 539.
[9] Delwaulle, François, and Wiemann, *Compt. rend.*, 1938, **206**, 1108; **207**, 340.
[10] Rolfe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

of the preceding paper, hold. From the experimental measurements, and the known constant for the formation of the pentabromide anion ($\chi_{3,5}$), $[Br_5^-]$ was calculated as before. $[Br_3^-]$ was then obtained from eqn. (4) of the preceding paper, and used with values of $[Br_2^F]$ and χ_3

$$[^{T}Br_C^-] = [^{b}Br_C^-] + [^{m}Br_C^-] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$[^{b}Br_C^-] = [Br_2^C] - [Br_5^-] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

cf. eqn. (6) of preceding paper.

$$[Br_F^-] = [Br_T^-] - [^{T}Br_C^-] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

to determine $[Br_F^-]$. The quantity $[^{m}Br_C^-]$ was then obtained from eqns. (1)—(3). The average ligand number $\bar{n} = [^{m}Br_C^-]/C_M$. Each experiment gave a single value of $\bar{n}$ and the corresponding value of $[Br_F^-]$.

(ii) *Spectroscopic Method.*—For a solution of optical density D in a cell d cm. long, a mean extinction coefficient ε_M can be defined by the relation,

$$D = \varepsilon_M \, . \, C_M \, . \, d$$

where C_M is the total concentration of the central group. If there are only mononuclear complexes present the mean extinction coefficient is a function of the free ligand concentration only.[11-13] Thus, solutions having the same value of ε_M must have the same value of [L] (" corresponding solutions "), and hence of $\bar{n}$. In order to minimise instrumental errors, Ahrland's technique [11] of working at a constant optical density was used; this method requires the use of at least two, and preferably more, absorption cells of accurately known length maintained at constant temperature. A modified Beckman DU spectrophotometer was used, and the design of the cells and their method of calibration are described elsewhere.[14] The ultraviolet absorption curve of mercuric bromide consists of a steep absorption step in the region 290—330 mμ, below which light transmission is negligible, and above which it is almost complete. There is, therefore, little latitude in the choice of wavelength. The constant optical density to be used was selected in the region of maximum sensitivity to concentration changes, namely $D = 0{\cdot}65$, and a wavelength of 310 mμ chosen to suit the available cells and the concentration range of mercuric bromide. At this wavelength, solutions of sodium bromide, sodium perchlorate, and perchloric acid are completely transparent. In addition, the absorption curve of mercuric bromide was not affected by the addition of perchlorates, suggesting that no complex formation occurs between mercuric bromide and perchlorate anions. Hence the solutions could safely be " loaded " with perchloric acid and sodium perchlorate to the acidity (0·01 molar) and ionic strength ($I = 0{\cdot}5$ on the molar scale) required. The molar scale was used instead of the molal scale used in the bromine indicator method. Pairs of solutions were prepared as follows: (*a*) C_L mmoles $l.^{-1}$ of sodium bromide, 10 mmoles $l.^{-1}$ of perchloric acid, and sodium perchlorate to $I = 0{\cdot}5$; (*b*) C_L mmoles $l.^{-1}$ of sodium bromide, 10 mmoles $l.^{-1}$ of perchloric acid, 15 mmoles $l.^{-1}$ of mercuric bromide, and sodium perchlorate to $I = 0{\cdot}5$, where $C_L = 20$, 15, 12, 10, 8, 6, and 4.

For each value of C_L, solutions (*a*) and (*b*) were mixed in the proportions to give the required optical density when placed in cells 0·5 cm., 1·0 cm., and 2·0 cm. long. An optical density of 0·65 could not be attained in the 0·5 cm. cell when $C_L = 6$ or 4 by mixing the above solutions, owing to the low concentration of mercuric bromide in (*b*) which could not be increased further because of the low solubility of mercuric bromide in the presence of such small quantities of excess of bromide. The omission of these readings did not affect the results seriously. It follows from the Beer–Lambert law that, for a given cell length, log ε_M should be linear with log C_M. It is therefore simple to obtain interpolated values of C_M corresponding to arbitrary values of ε_M. There is no simple relation between ε_M and C_L, corresponding values of these two quantities falling on a smooth curve, but it has been said [11] that a plot of ε_M/C_L against C_L is more nearly linear and therefore more suitable for interpolation. This was not so for the present results, so the simple plot of ε_M against C_L was used to obtain values of C_L corresponding to the arbitrarily selected values of ε_M. By this means, pairs of C_M, C_L values corresponding

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[11] Ahrland, *Acta Chem. Scand.*, 1949, **3**, 783.

[12] Olerup, Dissertation, Lund, 1944; quoted in ref. 11.

[13] Fronaeus, Dissertation, Lund, 1948; quoted in ref. 11.

[14] Richards, Scaife, and Tyrrell, to be published.

to a given ε_M were obtained, one pair for each cell length. If only mononuclear complexes are present, for solutions having the same ε_M value, C_M should be a linear function of C_L, though the fact that this is so does not entirely exclude the existence of polynuclear complexes. The slope of the line is equal to the average ligand number corresponding to the particular value of ε_M, and the intercept at $C_M = 0$ to the free ligand concentration [L].[15]

(iii) *Preparation of Materials.*—Mercuric bromide was purified by two successive sublimations of B.D.H. Laboratory Reagent Grade material. The other chemicals were purified as described in the preceding paper.

TABLE 1. *The system* $HgBr_2$–Br^- *at* 25° (*bromine indicator method*). *All concentrations are molal* × 10^3. *The sign* † *shows that the experiment was not used in the calculation of the formation constants.*

Expt.	$[Br_2^F]$*	$[Br_2^F]$	$[Br_2^T]$	$[Br_F^-]$	$[Br_T^-]$	C_M	$p[Br_F^-]$	$\bar{n}$
1 †	23·97	23·60	105·76	193·23	305·81	20·50	0·714	1·617
2 †	30·04	29·60	128·36	181·65	309·64	20·87	0·741	1·596
3 †	35·41	34·93	104·75	107·37	206·62	20·98	0·969	1·561
4 †	44·96	44·39	102·63	68·72	154·90	20·68	1·163	1·516
5	45·70	45·12	92·39	54·76	129·02	20·51	1·261	1·453
6	49·06	48·44	85·99	40·17	103·30	20·63	1·396	1·355
7	50·71	50·08	88·05	39·12	102·67	20·93	1·408	1·341
8	52·58	51·93	85·19	32·89	89·79	20·56	1·483	1·259
9	59·43	58·73	91·23	27·92	82·51	20·60	1·554	1·190
10	61·76	61·05	94·55	27·52	82·60	20·63	1·560	1·167
11	64·41	63·68	90·84	21·25	77·53	29·04	1·673	1·078
12	65·66	64·93	84·77	15·18	51·78	20·24	1·819	0·908
13	63·32	62·60	76·98	11·49	41·36	20·64	1·940	0·817
14	68·41	67·66	79·91	8·93	30·90	15·11	2·049	0·711
15	62·65	61·93	73·59	9·42	30·78	15·25	2·026	0·696
16	67·23	66·49	76·18	7·21	25·80	15·32	2·142	0·634
17	64·32	63·59	72·44	6·93	23·65	14·96	2·159	0·573
18 †	10·64	10·41	36·21	145·51	203·86	20·33	0·837	1·620
19 †	12·44	12·20	33·17	100·41	152·91	20·26	0·998	1·574
20 †	15·51	15·23	35·33	76·46	127·42	20·25	1·117	1·545
21	16·81	16·52	32·61	56·24	102·04	20·38	1·250	1·476
22	18·42	18·12	30·05	37·83	76·55	20·27	1·422	1·336
23	19·52	19·20	26·36	21·36	51·07	20·49	1·668	1·110
24 †	29·10	28·67	112·76	160·28	304·11	40·51	0·795	1·557
25 †	29·48	29·05	113·15	158·04	305·42	42·70	0·801	1·561
26 †	14·12	13·86	40·95	113·66	203·39	40·11	0·944	1·575
27	14·98	14·71	36·40	78·47	152·91	36·04	1·105	1·525
28	19·59	19·27	27·46	24·36	76·48	40·33	1·613	1·095

RESULTS

(i) *Bromine Indicator Method.*—As important conclusions can be drawn from the investigation at 25°, the results at this temperature are considered first (Table 1). The series 1—17 was done with an approximately constant total amount of bromine ($[Br_2^F]$ + $[Br_2^T]$) in the system, and by assuming $\chi_3 = 16{\cdot}85$ kg. mole^{-1}, and $\chi_{3,5} = 1{\cdot}50$ kg. mole^{-1} in the calculations. The total mercuric bromide concentration was also kept constant in most of the experiments at about 20 mmoles per 1000 g. of solvent. When the free bromide was relatively low, C_M was changed within the range 15—40 mmoles per 1000 g. of solvent without noticeable effect on the experimental formation curve. This is a necessary condition for the conclusion that only mononuclear complexes exist. A preliminary calculation of the constants of the system was attempted by plotting $\bar{n}/\{(\bar{n} - 1) . [L]\}$ against $(2 - \bar{n}) . [L]/(\bar{n} - 1)$.[16,17] The expected linear relation for a system containing only mononuclear complexes was found between these two functions, except for the three points corresponding to experiments 1, 2, and 3 (Table 1) which lay far from the main line (Fig. 1). A set of temporary constants was calculated from the best straight line (calculated by "least squares") through the remaining points, and the values used to calculate a formation curve. Points 1—3 lay below this curve, the deviations increasing as $p[Br_F^-]$

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[15] J. Bjerrum, "Metal Ammine Formation," P. Haase and Son, Copenhagen, 1941.

[16] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 1955, **9**, 1166.

[17] Irving and H. S. Rossotti, *J.*, 1953, 3397.

decreased, as illustrated in Fig. 2 where, however, the calculated formation curve has been obtained from the values of the association constants found by the methods described below, only the experimental points found at values of p[Br_F^-] > 1·2 being used. This was the value below which the experimental points diverged from the preliminary formation curve calculated from the temporary set of constants. When p[Br_F^-] was less than 1·2, the effect of changing either the bromine content or the mercuric bromide concentration was both noticeable and reproducible. A decrease in the total bromine in the system (using $\chi_3 = 16{\cdot}53$ kg. mole^{-1} and $\chi_{3,5} = 1{\cdot}45$ kg. mole^{-1}, the appropriate constants for the bromine concentration range used; see preceding paper) increased the apparent $\bar{n}$ value, while an increase in mercuric bromide concentration decreased it. Between p[Br_F^-] = 1·2 and 1·7 such changes had no definite effect on the results; the reproducibility near 1·7 was slightly less satisfactory than at lower values because a decrease in the bromine and an increase in the mercuric bromide concentration both tend to reduce the quantity [Br_2^O]. This is measured by difference, and the analytical errors become more important as [Br_2^F] approaches [Br_2^T]. When p[Br_F^-] > 1·7, it was not practicable to study the effect of changes in bromine or total mercuric bromide concentrations for this reason. However, the independent spectroscopic data fall quite closely on the extrapolated formation curve (Fig. 2), and confirm its general accuracy. It is reasonable to conclude that the deviations are only important for values of p[Br_F^-] below 1·2.

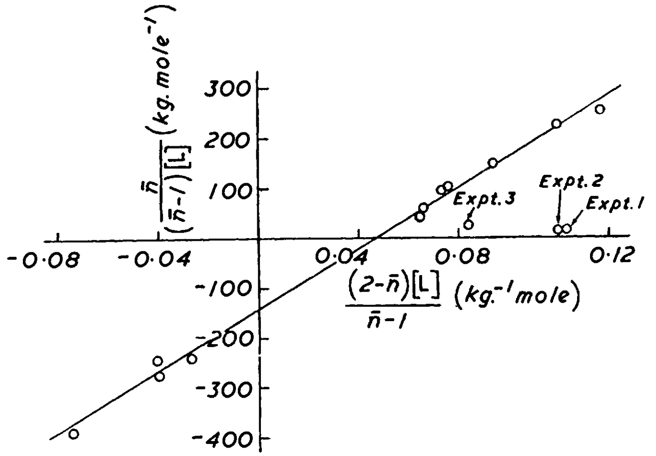

FIG. 1. *Preliminary calculation of formation constants at 25° by graphical method of Rossotti and Rossotti.*[16]

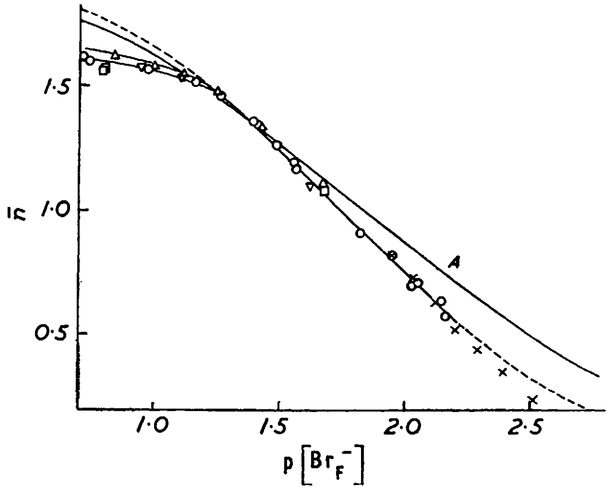

FIG. 2. *Formation curves at 25°.*

○ High bromine content.
□ ,, ,, (high C_M).
△ Low ,, ,,
▽ ,, ,, (high C_M).
× Spectroscopic data.

The full curves through the experimental points are apparent formation curves. The broken extensions at each end are obtained from formation constants calculated from experimental data obtained when p(Br_F^-) > 1·2. The curve calculated from Sillén's[6] formation constants is also shown as a full line, *A*.

The simplest explanation of these is that bromine forms donor–acceptor complexes with either $HgBr_3^-$ or $HgBr_4^{2-}$ or with both, according to the following equilibria:

$$HgBr_3^- + Br_2 \rightleftharpoons HgBr_5^- \quad \ldots \ldots \quad (3)$$

$$HgBr_4^{2-} + Br_2 \rightleftharpoons HgBr_6^{2-} \quad \ldots \ldots \quad (4)$$

The following symbolism is adopted: $m_n \equiv [HgBr_n]$, irrespective of charge; $b_n \equiv [Br_n]$, irrespective of charge; $a \equiv$ true free bromide concentration; $a' \equiv$ apparent free bromide concentration calculated without regard to the possible formation of $HgBr_5^-$ and $HgBr_6^{2-}$. Equilibrium constants (χ_3, $\chi_{3,5}$, $K_{2,3}$, $K_{3,4}$), defined in this and in the preceding paper, can be expressed in terms of this symbolism, as can the constants for the reactions (3) and (4), thus:

$$K_5 \equiv [HgBr_5^-]/[HgBr_3^-][Br_2] \equiv m_5/m_3b_2$$

$$K_6 \equiv [HgBr_6^{2-}]/[HgBr_4^{2-}][Br_2] \equiv m_6/m_4b_2$$

Using the method of calculation outlined above, which omits equilibria (3) and (4), we obtain an apparent average ligand number $\bar{n}$, and the apparent free bromide-ion concentration a' instead of the true values $\bar{n}_0$ and a respectively. It can be shown that, if equilibria (3) and (4) are included,

$$a' = a + (m_5 + m_6)/(1 + 2\chi_{3,5}b_2)\,\chi_3b_2$$

Hence $a' \geqslant a$, and $p[a'] \leqslant [a]$. The difference will not be large if m_5 and m_6 are small, and the difference between $p[a']$ and $p[a]$ will be even smaller. Again, it can be shown that,

$$\Delta\bar{n} \equiv (\bar{n} - \bar{n}_0) = \{m_6 - (m_5 + m_6)(\bar{n}_0 + \theta - 1)\}/C_M$$

where

$$\theta = \frac{1 + \chi_3b_2(1 + \chi_{3,5}\,b_2)}{\chi_3b_2(1 + 2\chi_{3,5}\,b_2)}$$

As can be seen, θ is a function only of the known constants of the bromine–bromide system, and of the free bromine concentration; it can therefore be calculated unequivocally. Now $\Delta\bar{n}$ is negative if

$$\bar{n}_0 + \theta - 1 > m_6/(m_5 + m_6)$$

Provided that $\theta > 2 - \bar{n}_0$, this inequality holds for all values of m_5 and m_6. In the present work, $(2 - \bar{n}_0)$ could be calculated from the extrapolated formation curve of Fig. 2, and θ was found always to be in excess of this quantity. Hence the observation that $\Delta\bar{n}$ was negative in the region where deviations were observed is consistent with the hypothesis that reactions (3) and (4) take part in the complex equilibria when bromide ions are in excess. It can be seen that

$$m_6 = K_{2,3}K_{3,4}K_6m_2a^2b_2$$

$$m_5 = K_{2,3}K_5m_2ab_2$$

Hence

$$\Delta\bar{n} = \frac{K_{2,3}ab_2[K_{3,4}K_6a - (K_{3,4}K_6a + K_5)(\bar{n}_0 + \theta - 1)}{1 + K_{2,3}a(1 + K_{3,4}a + K_5b_2 + K_{3,4}K_6ab_2)} \quad \ldots \quad (5)$$

If it is assumed that a' is a good approximation to a, $\bar{n}_0$ corresponding to a particular value of a can be obtained either by extrapolation from the formation curve of Fig. 1, or by an equivalent procedure from the equation,

$$\bar{n}_0 = K_{2,3}a + 2K_{2,3}K_{3,4}a^2/[(1 + K_{2,3}a + K_{2,3}K_{3,4}a^2)]$$

To use this, it is necessary to obtain $K_{2,3}$ and $K_{3,4}$ from experiments at relatively low free bromide concentrations. $\Delta\bar{n}$ can be got from $\bar{n}_0$ and the experimental $\bar{n}$ at the same free bromide concentration, and eqn. (5) then contains only two unknowns, K_5 and K_6. Data from experiments 1, 3, 25, 26 were used to obtain four equations of the form (5), and all

TABLE 2. *Calculated formation constants for the hypothetical complex ions* $HgBr_5^-$ *and* $HgBr_6^{2-}$ *at* 25°.

K_5 (kg. mole^{-1}) assuming $K_6 = 0$	10·8	9·5	3·7	5·3
K_6 (kg. mole^{-1}) assuming $K_5 = 0$	3·3	3·8	2·3	2·5

TABLE 3. *The system at* 35° (*bromine indicator method*). *All concentrations are molal* × 10^3. *The sign* † *indicates that the experiment was not used for the calculation of the formation constants.*

Expt.	$[\mathrm{Br_2^F}]$*	$[\mathrm{Br_2^F}]$	$[\mathrm{Br_2^T}]$	$[\mathrm{Br_F}^-]$	$[\mathrm{Br_T}^-]$	C_M	p$[\mathrm{Br_F}^-]$	$\bar{n}$
1 †	28·36	27·94	114·22	188·54	302·72	20·60	0·725	1·496
2 †	38·54	38·03	87·01	76·75	152·94	20·32	1·115	1·447
3 †	43·23	42·66	85·15	58·72	127·50	20·37	1·231	1·395
4	48·43	47·82	82·91	43·20	101·91	20·36	1·364	1·259
5	48·36	47·75	77·31	36·07	88·74	20·38	1·443	1·214
6	50·35	49·72	77·30	32·14	81·61	20·34	1·493	1·154
7	55·30	54·63	84·51	31·29	81·35	19·87	1·505	1·110
8	58·36	57·67	83·29	25·28	71·37	20·43	1·597	1·084
9	59·89	59·19	85·29	25·01	69·90	19·60	1·602	1·047
10	53·04	52·39	72·17	21·75	61·18	20·44	1·662	1·020
11	60·56	59·86	82·05	20·99	61·19	20·33	1·678	0·959
12	59·47	58·77	76·42	17·05	51·05	20·34	1·768	0·862
13	59·07	58·38	72·06	13·32	40·77	20·38	1·875	0·720
14	61·60	60·89	74·48	12·61	40·72	20·32	1·899	0·760
15	63·14	62·42	75·97	12·22	40·81	20·45	1·913	0·782

TABLE 4. *The system at* 5° (*bromine indicator method*). *All concentrations are molal* × 10^3. *The sign* † *indicates that the experiment was not used for the calculation of the formation constants.*

Expt.	$[\mathrm{Br_2^F}]$*	$[\mathrm{Br_2^F}]$	$[\mathrm{Br_2^T}]$	$[\mathrm{Br_F}^-]$	$[\mathrm{Br_T}^-]$	C_M	p$[\mathrm{Br_F}^-]$	$\bar{n}$
1 †	23·08	22·94	115·26	186·18	305·86	20·14	0·730	1·546
2 †	32·58	32·39	106·08	101·83	202·64	20·11	0·992	1·553
3 †	43·76	43·53	94·51	50·47	127·40	20·41	1·297	1·452
4	50·42	50·17	92·63	35·69	101·81	19·70	1·447	1·377
5	54·98	54·72	85·48	23·36	76·52	20·08	1·631	1·250
6	59·90	59·62	84·40	17·00	61·17	20·17	1·770	1·077
7	61·62	61·34	80·66	12·82	50·94	20·41	1·892	1·012
8	55·72	55·45	68·89	10·05	40·83	20·38	1·998	0·909
9	59·20	58·92	68·03	6·34	25·44	15·55	2·198	0·697

six possible solutions of these equations taken in pairs were obtained. Every estimate of K_6 was positive, but five out of six estimates of K_5 were negative. This suggests that it is incorrect to assume the simultaneous formation of both $HgBr_5^-$ and $HgBr_6^{2-}$. If K_6 is taken as zero, it is possible to estimate K_5 from eqn. (5) when no $HgBr_6^{2-}$ is present; similarly K_6 can be obtained by assuming K_5 to be zero. The resulting "constants" are shown in Table 2. From the much smaller variations of K_6 than of K_5, it seems more reasonable to assume that only $HgBr_6^{2-}$ is present; this would be expected for a donor–acceptor complex of the kind suggested. Although the estimate of K_6 as about 3 kg. mole^{-1} cannot be very accurate because of uncertainties in $\Delta\bar{n}$, it must be of the correct order of magnitude, if, as seems likely, the general explanation of the deviations given here is correct. Similar deviations at low p$[\mathrm{Br_F}^-]$ values were observed at 5° and 35° but were not examined in detail. The full experimental results at these temperatures are given in Tables 3 and 4. The appropriate hydrolysis corrections were applied as described in the preceding paper.

(ii) *Spectroscopic Method* (25° *only*).—Figs. 3 and 4 show the variation of log ε_M with log C_M, and of ε_M with C_L respectively, for the three cells used. These had previously been calibrated as described elsewhere [14] in terms of the 0·5 cm. cell as a standard, by use of potassium nitrate solutions. Corresponding values of C_M and C_L at constant ε_M, interpolated from these graphs, are shown in Table 5, together with the derived $[\mathrm{Br_F}^-]$ and $\bar{n}$ pairs. The plots of C_L against C_M at constant ε_M from which these were derived were linear, as expected if polynuclear complexes were absent. This is not however a particularly sensitive test for the detection of small quantities of polynuclear complexes, but further investigation, at other wavelengths, was not practicable because of the unfavourable form of the absorption curve. Nor was it practicable to extend the experiments to higher free bromide concentrations; the variation of ε_M with increasing C_L became so small as the maximum value of ε_M was approached that accurate interpolation in the C_L–ε_M curve became impossible. The experimental points are shown in Fig. 2 and agree well with those obtained by the other method.

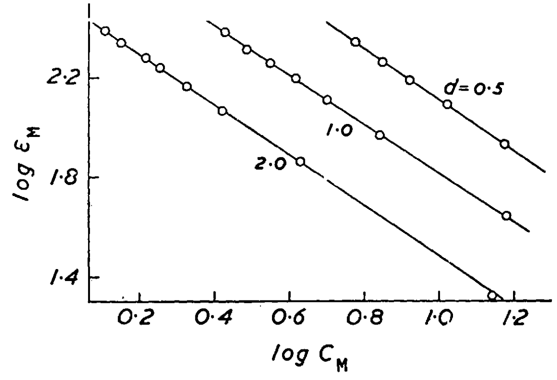

FIG. 3. log ε_M *as a function of* log C_M *at* 25° *at various values of d (cm.).*

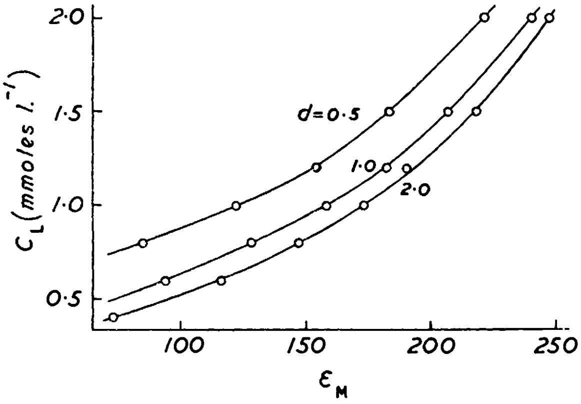

FIG. 4. C_L *as a function of* ε_M *at* 25°, *at various values of d (cm.).*

TABLE 5. *Spectroscopic study of the system at* 25°. *All concentrations are molal* × 10^3 (*d* = *cell length*).

	d = 0·500 cm.		*d* = 0·997 cm.		*d* = 2·09 cm.			
ε_M	C_M	C_L	C_M	C_L	C_M	C_L	[L] = $[Br_F^-]$	n
80	15·85	7·8	8·09	5·4	3·87	4·3	3·1	0·29
100	12·74	8·7	6·47	6·3	3·11	5·2	4·1	0·35
120	10·64	9·8	5·37	7·4	2·57	6·3	5·1	0·44
140	9·16	11·1	4·62	8·7	2·23	7·5	6·3	0·52
160	8·02	12·7	4·01	10·1	1·95	8·9	7·6	0·63
180	7·16	14·6	3·56	11·9	1·73	10·7	9·3	0·73
200	6·49	16·9	3·21	14·1	1·57	12·8	11·5	0·82

Calculation of the Complexity Constants.—There are many methods available, and the use of a graphical one for the bromine indicator data at 25° has already been mentioned. This is satisfactory except for values of $\bar{n}$ near unity where experimental errors become exaggerated. For a system in which only two successive complexes are formed

$$\bar{n} + (\bar{n} - 1)[Br_F^-]K_{2,3} + (\bar{n} - 2)[Br_F^-]^2 K_{2,3}K_{3,4} = 0 \quad . \quad . \quad . \quad (6)$$

There are two unknowns, and $K_{2,3}K_{3,4}$ could be obtained in principle from two points on the formation curve. However there are usually more data than the minimum, and the problem is to combine them. A general method would be to solve eqn. (5) by using all possible pairs of points in turn; this is laborious and points close together would be badly conditioned. Consequently, twelve experimental pairs of ($\bar{n}$,[$\mathrm{Br_F}^-$]) values were arranged in order of increasing $\bar{n}$, and the first and seventh, second and eighth, etc., pairs substituted in turn into eqn. (5), and solved for $K_{2,3}$, $K_{3,4}$. As before this general method is unsatisfactory when $\bar{n}$ is near unity. The third method used was based on the observation that, within the range of p[$\mathrm{Br_F}^-$] values for which the formation of $\mathrm{HgBr_6}^{2-}$ can be neglected, $\bar{n}$ was almost linear with p[$\mathrm{Br_F}^-$](a). The best straight line through these experimental points was obtained by the least-squares method by assuming the error to lie entirely in n, and the standard deviation of $\bar{n}$ ($\sigma_{\bar{n}}$) calculated. Two points were selected at arbitrary values of a near the extreme ends of the true formation curve and assumed to be in error by $\pm\sigma_{\bar{n}}$. By solving eqn. (5) with pairs of points ($\bar{n}_1 + \sigma_{\bar{n}}$, a), ($\bar{n}_2 - \sigma_{\bar{n}}$, a_2), and ($\bar{n}_1 - \sigma_{\bar{n}}$, a_1), ($\bar{n}_2 + \sigma_{\bar{n}}$, a_2), a range of values for $K_{2,3}$ and $K_{3,4}$ was obtained from which an estimate of the mean, and of the likely, error of each constant could be calculated. Points near the ends of the calculated straight line were chosen partly because the true formation curve should coincide most closely with the straight line at the ends and in the centre, and partly because the term (n — 1) is then as large as possible. By using the calculated constants from these selected points the true formation curve could be found. It was so nearly linear in the region of p[$\mathrm{Br_F}^-$] used, that the standard deviation of the experimental $\bar{n}$ values from the least-squares line was identical with that from the true formation curve. This completely justifies the use of the linear approximation method for this case.

TABLE 6. *Formation constants of the system at 25° calculated by different methods from the data in Table* 1.

Method	$K_{2,3}$ (kg. mole^{-1})	$K_{2,3}K_{3,4}$ (kg.^{2} mole^{-2})
Graphical, see refs. 16, 17	136	3030
Solution of pairs of simultaneous equations	139 with standard deviation 13	3050 with standard deviation 160
Linear approximation method	135 ± 10	3060 ± 200

The results of the three methods of calculating the formation constants are shown in Table 6. The previous potentiometric study at 25° at almost the same ionic strength and acidity[6] gave $K_{2,3} = 260 \pm 70$ l. mole^{-1}, $K_{2,3}K_{3,4} = 4700 \pm 200$ l.^{2} mole^{-2}; the formation curve calculated from these figures is shown in Fig. 2.

The linear approximation method alone was used on the data obtained at 5° and 35°, since the experimental formation curves were substantially linear in the regions where there was no appreciable interaction between the competing complex systems. The values excluded from the calculations are indicated in Tables 3 and 4. It was found that the complexity constants had the following values: (a) at 5° $K_{2,3} = 230 \pm 25$ kg. mole^{-1}; $K_{2,3}K_{3,4} = 5900 \pm 600$ kg.^{2} mole^{-2}; (b) at 35° $K_{2,3} = 110 \pm 20$ kg. mole^{-1}; $K_{2,3}K_{3,4} = 2000 \pm 250$ kg.^{2} mole^{-2}. No attempt to calculate the constants K_5 or K_6 was made at these temperatures.

The results of the spectroscopic investigation at 25° were used to calculate complexity constants by the first method described above. A satisfactory straight line was obtained and gave the following constants: $K_{2,3} = 100$ l. mole^{-1}; $K_{2,3}K_{3,4} = 4000$ l.^{2} mole^{-2}. In view of the limited concentration range to which the observations were limited these values are not as satisfactory as those found by using the bromine indicator method.

Calculation of the Thermodynamic Functions of the System.—The thermodynamic complexity constants (K^{T}) are related to the experimental constants by the equations:

$$K_{2,3}{}^{\mathrm{T}} = K_{2,3} \cdot \frac{\gamma_{\mathrm{HgBr_3^-}}}{\gamma_{\mathrm{Br^-}} \cdot \gamma_{\mathrm{HgBr_2}}}; \quad K_{3,4}{}^{\mathrm{T}} = K_{3,4} \cdot \frac{\gamma_{\mathrm{HgBr_4^{2-}}}}{\gamma_{\mathrm{Br^-}} \cdot \gamma_{\mathrm{HgBr_3^-}}}$$

where γ are the activity coefficients on the molal scale.

If $\Delta G^{\text{app.}}$, $\Delta H^{\text{app.}}$, and $\Delta S^{\text{app.}}$ are the quantities obtained by the usual methods from the experimental constants and their variation with temperature, and ΔG°, ΔH°, and ΔS° are the corresponding changes for the hypothetical ideal reference system when products and reactants are at unit molality, it can be shown [18] that

$$\Delta G^{\text{app.}} = \Delta G^\circ - \sum_i \nu_i \ln \gamma_i$$

$$\Delta H^{\text{app.}} = \Delta H^\circ - \boldsymbol{R}T^2\sum_i \nu_i\, \partial/\partial T(\ln \gamma_i)$$

$$\Delta S^{\text{app.}} = \Delta S^\circ - \boldsymbol{R}[T\sum_i \nu_i\, \partial/\partial T(\ln \gamma_i) + \sum_i \nu_i \ln \gamma_i]$$

The quantities ν_i are the stoicheiometric coefficients of the components taking part in the reaction. In sufficiently dilute solution the activity coefficients could be calculated from an extended form of the Debye–Hückel equation, such as that [19] due to Davies, $-\log \gamma_i = Az_i^2\{[\sqrt{I}/(1 + \sqrt{I})] - 0{\cdot}2I\}$. Strictly, this is not valid at $I = 0{\cdot}5$ but will be used to obtain some idea of the corrections required for the deviations from ideal behaviour. The temperature coefficient of the activity coefficient can be estimated from the known variation in A with temperature, or by a method formerly suggested by one of us.[20] In either case the approximate relation $\partial/\partial T\ (\log \gamma_i) = 2 \times 10^{-3} \log \gamma_i$ is found to hold at room temperature. The constant A has, for this purpose, been assumed to vary with temperature in the same way as the corresponding coefficient of the Debye–Hückel equation.

The activity coefficient correction to $K_{2,3}$, and to the quantities derived therefrom, will, according to this, depend only on the activity coefficient of the neutral molecule $HgBr_2$. This is unlikely to be far from unity, and the apparent changes in the thermodynamic functions G, H, and S can be equated to the standard state changes without serious error. For $K_{3,4}$ the apparent entropy change exceeds the true standard state entropy change by about 2 entropy units; this correction is probably small in comparison with the errors involved in the calculation of entropy changes by this method.

When $\log K_{2,3}$ was plotted against $1/T$, a satisfactory straight line was obtained from the slope of which $\Delta H_3^{\text{app.}}$ was found to be $-4{\cdot}3$ kcal. mole^{-1}. $\Delta G_{2,3}^{\text{app.}}$ at 5°, 25°, and 35° can be calculated as $-3{\cdot}01$, $-2{\cdot}91$, and $-2{\cdot}86$ kcal. mole^{-1} respectively. From these figures $\Delta S_{2,3}^{\text{app.}}$ can be calculated to be -5 e.u. According to the above arguments,

$$\Delta S_{2,3}{}^\circ = \Delta S_{2,3}{}^{\text{app.}} = -5 \text{ e.u.}$$

The plot of $\log (K_{2,3}K_{3,4})$ against the reciprocal of the temperature was not quite linear, but from the average slope the apparent heat content change for the overall reaction to form $HgBr_4^{2-}$ was found to be $-6{\cdot}2$ kcal. mole^{-1} and the corresponding entropy change to be between -4 and -5 e.u. The apparent entropy change for the reaction $HgBr_3^- + Br^- \longrightarrow HgBr_4^{2-}$ must therefore be close to zero. $\Delta S_{3,4}{}^\circ$ is therefore assigned the value -2 e.u. In all these calculations the equilibrium constants used were those obtained from the formation curves by the linear approximation method.

DISCUSSION

The measurements at 25° by the bromine indicator method were done in conditions differing from those used in the earlier potentiometric measurements only in that concentrations were expressed on a molal, rather than a molar scale. An approximate calculation, the density of the solutions being assumed to be about 1·05, shows that $K_{2,3}$ calculated on a molal scale should be about 0·95 of that calculated on a molar scale. The corresponding factor for $K_{2,3}K_{3,4}$ is about 0·90. The constants obtained in the earlier work [6] when converted to a molal basis using these constants are therefore appreciably larger than

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[18] Prigogine and Defay, "Chemical Thermodynamics," trans. Everett, Longmans, Green and Co. Ltd., London, 1952.

[19] Davies, *J.*, 1938, 2093.

[20] Tyrrell and Hollis, *Trans. Faraday Soc.*, 1952, **48**, 893.

those derived from the present measurements. The effect on the formation curve of the change in concentration scale is very small, and cannot account for the difference illustrated in Fig. 2. The curve calculated from the earlier results coincides with that derived from the present measurements where $\bar{n}$ is large and $p[Br_F^-]$ small. This is just the concentration range to which the potentiometric measurements were restricted, and the discrepancy between the two sets of constants is presumably due very largely to the fact that a wider range of free bromide concentrations has been studied in this work. The excellent agreement of the two formation curves near the upper end justifies the assumption that, for $p[Br_F^-] > 1{\cdot}2$, the bromine–bromide and mercuric bromide–bromide equilibria can be considered as independent. If this had not been so, these curves could not have coincided so well. At high $p[Br^-_F]$ values the spectroscopic measurements fall on or near the extrapolated formation curve, and the constants derived from these alone are close to, though not quite identical with, those obtained by the bromine indicator method. It can fairly be claimed that the constants given in Table 6 are the most satisfactory ones at present available * for 25°. No independent data are available at the other temperatures studied.

TABLE 7. *Standard entropies of mercuric bromide complexes (e.u.).*

Species	$HgBr_2$	$HgBr_3^-$	$HgBr_4^{2-}$
Observed entropy	41	55	75
Calculated entropy	30	61	39

The entropy of solution of undissociated mercuric bromide can be calculated without serious error from the heat of solution and the solubility of mercuric bromide in water. At 25° a saturated solution of mercuric bromide contains 0·609 g. per 100 g. of water.[21, 22] Corrections for dissociation are negligible, and the activity coefficient of mercuric bromide in the saturated solution can be assumed to be unity. The standard Gibbs free energy change on solution can then be calculated to be $+2{\cdot}4$ kcal. mole^{-1}. The heat of solution [23] to form a saturated solution is $+3{\cdot}4$ kcal. mole^{-1}. Corrections for dissociation are again negligible, and the measured heat being assumed to be equal to the standard heat of solution, the standard entropy of solution at 25° is $+3{\cdot}5$ e.u. Accepting Latimer's estimate of 37·2 e.u. for the entropy of solid mercuric bromide,[24] we find that the standard entropy of undissociated mercuric bromide in water is 41 e.u. From this and the observed entropy changes, standard entropies for the ions $HgBr_3^-$ and $HgBr_4^{2-}$ can be calculated. These are shown in Table 7 together with the values calculated by the empirical methods suggested by Cobble.[25]

There are several points of interest. For the neutral molecule the experimental value is appreciably greater than the calculated one. The first is more reasonable, since, from it and the known entropies of the aqueous mercuric ($-5{\cdot}4$ e.u.) and bromide (19·25 e.u.) ions [26] the standard entropy change for the reaction,

$$Hg^{++}, aq. + 2\,Br^-, aq. \longrightarrow HgBr_2, aq.$$

can be calculated to be $+8$ e.u. From Cobble's figure, the unlikely value of -3 e.u. would be obtained. The experimental entropy of $HgBr_4^{2-}$ is much greater than the calculated one; a similar discrepancy has been noted by Cobble [25] between the calculated value and

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* *Added, October 11th,* 1957.—The results of a liquid-phase partition study at 25° of the complexes have now appeared (Marcus, *Acta Chem. Scand.*, 1957, **11**, 599). The constants differ slightly both from the present results and from those of Sillén and his co-workers.

[21] Garrett, *J. Amer. Chem. Soc.*, 1939, **61**, 2744.

[22] Tyrrell and Richards, *J.*, 1953, 3812.

[23] Berthelot, see Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Hw. II, 1556.

[24] Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, 2nd Edn., 1952.

[25] Cobble, *J. Chem. Phys.*, 1953, **21**, 1443, 1446.

[26] Powell and Latimer, *ibid.*, 1951, **19**, 1139.

that quoted by Latimer[24] which was based on the older data of Sherrill. Whatever the reason for this difference, it is surprising to find that $HgBr_4^{2-}$ apparently has a larger entropy than the singly charged species $HgBr_3^-$. The difference is so great that it can scarcely be attributed entirely to experimental errors in the temperature coefficients of the formation constants. It can be reduced, though not changed in sign, if it is assumed that the singly charged ion has a water molecule co-ordinated in its inner co-ordination sphere. The formation reaction is then

$$HgBr_2 + Br^- + H_2O \longrightarrow Hg[Br_3,H_2O]^-$$

The entropy of liquid water being assumed to be 17 e.u., the standard entropy of the singly charged complex ion becomes 72 e.u. This improvement lends some support to the view that when mercuric bromide co-ordinates with a bromide ion the linear (*sp*) hybridisation in the neutral molecule changes directly to tetrahedral (sp^3) hybridisation, the vacant site being occupied by a water molecule. This was suggested by Woodward[10] on the basis of Raman-effect measurements.

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