71. *Equilibrium Constants for the Reaction between Bromine and Bromide Ions at 5°, 25°, and 35° in Aqueous Medium of Constant Ionic Strength and Acidity.*

By D. B. Scaife and H. J. V. Tyrrell.

Bromine combines with bromide ions to form principally the tribromide ion Br_3^-, and this reaction can be used to measure free bromide-ion concentrations in other complex equilibria involving bromide ions provided that the formation constants for the bromine–bromide ion system are known with sufficient accuracy. The precise measurement of these constants at an ionic strength of $I = 0{\cdot}5$ and an acid concentration of 0·01 molal at three temperatures is described. This was a necessary preliminary to the study of the mercuric bromide–bromide ion system reported in the succeeding paper.

Bromine forms donor–acceptor complexes with bromide ions of the forms Br_3^- and Br_5^-, the former being the more important. The concentration of free bromine in a solution containing both bromine and bromide ions can be accurately determined by allowing the bromine to come to equilibrium, through the vapour phase, with a similar solution not containing bromide ions. The equilibrium activity of bromine in this solution is equal to the activity of free bromine in the solution containing bromide ions. If the activity coefficients are known, or are the same in both solutions, the concentration of the free bromine in the complexed solution can be found easily and precisely, by analysing the bromide-free solution. This was the basis of a method used in earlier studies of this equilibrium system.[1, 2] If the constants for this system can be found with sufficient accuracy, the concentration of free bromide ions in a solution containing both bromine and bromide ions can be calculated. Thus, the bromine–bromide ion system could, in principle, be used to study other complex equilibria involving bromide ions by adding bromine to the mixture, measuring the total and free bromine concentrations, and using these to calculate the free bromide-ion concentration. This method is more laborious than direct measurement of the free bromide-ion concentration, for example, with an electrode system reversible to bromide ions, but is valuable where such methods cannot be applied. Its development required accurate measurements of the equilibrium constants of the bromine–bromide ion system under the appropriate experimental conditions as now described; an application is described in the following paper.

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[1] Warley, *J.*, 1905, **88**, 1107.

[2] Jones and Baeckström, *J. Amer. Chem. Soc.*, 1934, **56**, 1517.

The main product in the reaction between bromine and bromide ions is the tribromide ion:

$$Br_2 + Br^- \rightleftharpoons Br_3^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

An equilibrium constant χ_3 can be defined for this reaction as

$$\chi_3 = [Br_3^-]/([Br_2][Br^-])$$

However, earlier studies,[1,3,4] culminating in that of Jones and Baeckström,[2] showed that the following reactions cannot always be neglected:

$$2Br_2 + Br^- \rightleftharpoons Br_5^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HBrO \quad . \; . \; . \; . \; . \quad (3)$$

For these, equilibrium constants χ_5 and χ_h can be defined as follows:

$$\chi_5 = [Br_5^-]/([Br^-][Br_2]^2)$$

$$\chi_h = [H^+][Br^-][HBrO]/[Br_2]$$

In much earlier work activity coefficients were neglected; later they were included [2,4] by using data on the activity coefficient of bromine in salt solutions in which no complex formation occurred, and assuming the activity coefficients of the singly charged species Br^-, Br_3^- to be equal as a first approximation. In all our experiments, a solvent medium of constant acidity and of high and almost constant ionic strength was used. The slight acidity helps to suppress the hydrolysis reaction (3), and the constant ionic strength to ensure that activity coefficients are independent of changes in concentration of the complex species. Since the main object was to use the equilibrium constants to study the mercuric bromide–bromide ion system, the conditions used were those which had been adopted in the only previous modern study [5] of this system, except that the molal scale of concentration replaced the molar one. All solutions were therefore 0·01 molal in perchloric acid, and a total ionic strength of $I = 0{\cdot}5$ was maintained by addition of sufficient sodium perchlorate. The equilibrium was examined for concentration ranges which were of use in the investigation of the mercuric bromide–bromide ion system, namely 20—300 mmoles of sodium bromide per 1000 g. of solvent and at bromine concentrations which gave equilibrium concentration differences between the bromide-rich and bromide-free solutions which could be measured with reasonable accuracy.

EXPERIMENTAL

A glass equilibrator, very similar to Jones and Kaplan's,[6] was used to measure the equilibrium distribution of bromine between the bromide-rich and bromide-free solutions. The apparatus is so constructed that rotation about an axis inclined at a small angle to the vertical causes the vapour to circulate through each solution in turn while preventing direct contact between them. Each separate solution compartment could be filled and emptied through ground-joints normally closed with a stopper lubricated with Fluorolube W grease. It was necessary to rotate the equilibrator in a constant-temperature bath (±0·1° or better) for 48 hr. to ensure that equilibrium had been attained at all temperatures used.

About 100 g. each of the following solutions were prepared for each experiment: (i) *x* mmoles of sodium bromide, 10 mmoles of perchloric acid per 1000 g. of water, and sufficient sodium perchlorate to give an ionic strength of 0·5 on the molality scale, and (ii) as (i) without sodium bromide.

A total of 12—14 mmoles of liquid bromine were usually added to both solutions in approximately the proportions expected to be present after equilibration. The solutions were

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[3] Jakowkin, *Z. phys. Chem.*, 1895, **18**, 585; 1896, **20**, 193; Lewis and Randall, *J. Amer. Chem. Soc.*, 1916, **38**, 2348; Linhart, *ibid.*, 1918, **40**, 158; Jones and Hartmann, *Trans. Amer. Electrochem. Soc.*, 1916, **30**, 295; Bray and Connolly, *J. Amer. Chem. Soc.*, 1911, **33**, 1485; Lewis and Storch, *ibid.*, 1917, **39**, 2544; Sherrill and Izard, *ibid.*, 1928, **50**, 1665.

[4] Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, 1932, **28**, 101.

[5] Bethge, Jonevall-Westöö, and Sillén, *Acta Chem. Scand.*, 1948, **2**, 828.

[6] Jones and Kaplan, *J. Amer. Chem. Soc.*, 1928, **50**, 1600.

then put in the two sides of the equilibrator which was allowed to come to thermal equilibrium in the thermostat before inserting the stoppers. After 48 hours' rotation, the contents were analysed. To obtain consistent results Jones and Baeckström's methods [2] were modified. The contents of both compartments were forced simultaneously into separate receivers with compressed air saturated with bromine vapour to approximately the equilibrium pressure; the first few ml. were discarded, the bulk of the rest passed into collecting flasks, fitted with side-arms of the type designed by Jones and Baeckström, and a little was left in the equilibrator. If samples were removed successively from the equilibrator, a slight progressive loss of bromine occurred. The collecting flask contained about 20 ml. of saturated sodium iodide solution, and the side arm was packed with small glass helices moistened with the same solution and a little solid sodium hydrogen carbonate. As the receiving flasks were filled the air was displaced through the side arm, any trace of bromine vapour in it being trapped by the iodide solution. When the addition of the bromine solution was complete, the acid solution in the flask was neutralised by tilting it so that the contents ran into the side arm and reacted with the solid hydrogen carbonate. Preliminary experiments showed that the excess of iodide was oxidised sufficiently rapidly in acid solution, by dissolved air, to give inaccurate results unless the contents of the flask were neutralised immediately after addition of the bromine solution. Addition of this to an initially alkaline iodide solution also gave anomalous results (cf. ref. 2). The weight of bromine solution added was found by weighing the receiver immediately before adding the bromine solution, and again after neutralisation. The loss of weight due to evolution of carbon dioxide in the neutralisation was negligible (about 10 mg., or 25% of the theoretical amount, in a total solution weight of over 100 g.). Since the weight of the contents of the flask, including those of the side arm, had been found initially, the weight dilution factor of the transferred bromine solution could be determined. After estimating each iodine solution in terms of the concentration per 1000 g. of solution, we found the concentration of bromine in a known weight of the original solution at equilibrium by using this weight dilution factor. Since the weight of the other constituents in the original solution was known these bromine concentrations could easily be converted to the molal scale which was used throughout.

The iodine liberated from the sodium iodide was estimated by weight titration with a standard sodium arsenite solution in presence of a sodium hydrogen carbonate buffer. A sample of the iodine solution was weighed into a flask containing about 2 g. of solid sodium hydrogen carbonate, and a sodium arsenite solution, containing about 0·075 equiv. per 1000 g. of solution, added from a simple weight burette until the solution was pale yellow. The remaining iodine was estimated by adding sodium arsenite solution of about one fifth of the concentration of that used for the bulk of the titration, from a microburette, starch solution being used as indicator. The density of this dilute solution was assumed to be unity, and the volume added equal to the weight. The standard arsenite solution was prepared from "AnalaR" arsenic oxide by Vogel's method,[7] except that the solution was made up to a known total weight. Three estimations were carried out on each iodine solution, the spread being always less than 0·1%.

Sodium bromide, B.D.H. Laboratory Reagent grade, was recrystallised thrice from distilled water, and the resulting hydrated crystals dehydrated over sodium hydroxide in a vacuum desiccator. Sodium perchlorate, B.D.H. Laboratory Reagent grade, contains principally chloride as an impurity which was effectively removed by recrystallisation twice at 80°. The anhydrous salt thus formed was dried (NaOH). "AnalaR" perchloric acid was used without purification; the solutions used in the equilibrator were made up by adding known weights of a diluted stock solution of known molality. Bromine was prepared from "AnalaR" potassium bromide by oxidation with chromic acid and distillation.[8] The initial 1% of distillate contained iodine from any iodide impurities present in the bromide, and was discarded. Sufficient chromic acid for the oxidation of about 95% of the bromide present was added in all; any chloride impurities remained unoxidised and the bulk of the bromine collected was therefore free from both chlorine and iodine.

THEORY

In solutions containing bromide ions, particularly when they are slightly acid, the hydrolysis reaction (3) can be neglected. This was not true for the bromide-free solutions.

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[7] Vogel, "Quantitative Inorganic Analysis," p. 416, Longmans, Green and Co., London, 1943.

[8] Robinson and Briscoe, *J.*, 1925, **127**, 142.

However there are no data on the appropriate hydrolysis constants for the conditions used here, and the necessary correction was made as follows. Initially only reactions (1) and (2) are considered, with the following notation: $[Br_2^F] \equiv$ concentration of free bromine in the complexing solution (= measured concentration of bromine in the bromide-free solution if hydrolysis is neglected); $[Br_2^T] \equiv$ total concentration of bromine in the complexing solution; $[Br_2^C] = [Br_2^T] - [Br_2^F] \equiv$ concentration of combined bromine, obtained directly from the measured quantities; $[Br_T^-] \equiv$ known total bromide concentration in the complexing solution; $[Br_C^-] \equiv$ combined bromide-ion concentration; and $[Br_F^-] \equiv$ free bromide-ion concentration.

It is obvious that

$$[Br_3^-] = [Br_2^C] - 2[Br_5^-] \qquad (4)$$

$$[Br_C^-] = [Br_3^-] + [Br_5^-] \qquad (5)$$

From eqn. (4) and (5) it follows that

$$[Br_C^-] = [Br_2^C] - [Br_5^-] \qquad (6)$$

Also,

$$[Br_F^-] = [Br_T^-] - [Br_C^-] \qquad (7)$$

From eqn. (4) and the definition

$$\chi_{3,5} = \chi_5/\chi_3 \qquad (8)$$

it can be seen that

$$[Br_5^-] = [Br_3^-][Br_2^F] \cdot \chi_{3,5} \qquad (9)$$

Extension of this argument shows that the following relation must exist:

$$\alpha = -\beta \cdot \chi_{3,5} + 1/\chi_3 \qquad (10)$$

where α and β are defined as the following combinations of experimentally accessible quantities:

$$\alpha \equiv \frac{[Br_2^F]([Br_T^-] - [Br_2^C])}{[Br_2^C]}$$

$$\beta \equiv \frac{[Br_2^F]^2(2[Br_T^-] - [Br_2^C])}{[Br_2^C]}$$

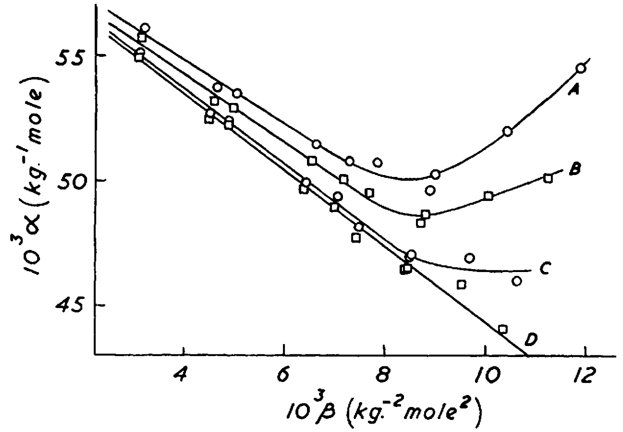
If the ionic strength, and hence the activity coefficients are kept constant throughout, both $\chi_{3,5}$ and χ_3 are true constants, and a plot of α against β should be straight. When the measured concentration of bromine in the bromide-free solution was identified with $[Br_2^F]$ it was found that this was not so. This was because some hydrolysis occurred in the bromide-free solution according to reaction (3), accompanied by complex formation between the liberated bromide ions and the bromine present. However the hydrolysed and complexed bromine, together with the free bromine, were all analysed as bromine in an amount which may be designated as $[Br_2^F]^*$. This was greater than the true free bromine concentration $[Br_2^F]$, and it was the use of $[Br_2^F]^*$ instead of $[Br_2^F]$ which led to the observed deviations from linearity in the plot of α against β. With an approximate value for χ_3 and trial values of χ_h it was possible to apply a correction to $[Br_2^F]^*$, the appropriate value of χ_h selected being that which made α a linear function of β. According to eqn. (10), the slope of this line should be $-\chi_{3,5}$, and the intercept $1/\chi_3$. In practice, it was found preferable to calculate values of χ_3 as follows. Using the value of $\chi_{3,5}$ obtained from the slope, we calculated $[Br_5^-]$ for a given experiment from eqn. (9). Using this, we obtained $[Br_3^-]$ from eqn. (4), and the free bromide concentration from (6) and (7). A value for χ_3 was then calculated. A series of experimental observations led to a set of values of χ_3 from which the mean and the standard deviation of the mean were estimated.

RESULTS

(i) *At 25°.*—The results for this temperature are displayed in Table 1. Columns 1, 3, and 8 are the experimental quantities. If no correction was made for hydrolysis, the relation between

α and β was not linear (Figure, curve *A*). Using an approximate value of $\chi_3 = 17$ kg. mole^{-1} and the following hydrolysis constants in turn: $5{\cdot}9 \times 10^{-9}$ kg.$^{-2}$ mol.^{2} (experimental, Jones and Baeckström [2]), four times this value, and six times this value, we obtained curves *B*, *C*, and *D* of the Figure. As the hydrolysis correction was increased, the plot of α against β tended towards linearity, and became satisfactorily linear in curve *D*. Although the correction used was some six times that expected from Jones and Baeckström's experimental value for the hydrolysis, it has been employed here to correct $[Br_2{}^F]^*$ to the $[Br_2{}^F]$ figures shown in column 2 of Table 1. Only by this means could the principal equilibria be put in the simple form covered by reactions (1) and (2). Clearly the " hydrolysis correction " must include an adjustment made necessary by other, unknown, side reactions. The best straight line was calculated from the method of averages for the data represented by curve *D* and the slope gave $\chi_{3,5} = 1{\cdot}50$ kg. mole^{-1}. Each experimental point was then used to calculate a separate value of χ_3. From the resulting ten values a mean of 16·85 kg. mole^{-1} with a standard deviation of the mean of 0·09 was calculated. Hence $\chi_5 = 25{\cdot}3$ kg.^{2} mole^{-2}. For the present purpose it is not necessary to know $\chi_{3,5}$ with great accuracy; the above figure is probably not more than 2% in error. Some experiments at lower total bromine concentrations gave the results shown at the bottom of Table 1; a similar " hydrolysis correction " was needed for these also. For these four experiments $\chi_{3,5}$ was found to be 1·45 kg. mole^{-1} and the mean value of $\chi_3 = 16{\cdot}53$ kg. mole^{-1}. This small but definite difference has not yet been explained, and in the

Influence of hydrolysis corrections at 25°



Curve *A*. (○) Uncorrected data.
Curve *B*. (□) Corrected, by using $\chi_h = 5{\cdot}9 \times 10^{-9}$ kg.$^{-2}$ mole^2.
Curve *C*. (○) Corrected, by using $\chi_h = 23{\cdot}6 \times 10^{-9}$ kg.$^{-2}$ mole^2.
Curve *D*. (□) Corrected, by using $\chi_h = 35{\cdot}4 \times 10^{-9}$ kg.$^{-2}$ mole^2.

TABLE 1. *Determination of* χ_3 *at* 25°. *All concentrations are molal* × 10^3.
Units of χ_3 *are kg. of solvent mole*$^{-1}$.

$[Br_2{}^F]^*$	$[Br_2{}^F]$	$[Br_2{}^T]$	$[Br_2{}^C]$	$[Br_5{}^-]$	$[Br_3{}^-]$	$[Br_C{}^-]$	$[Br_T{}^-]$	$[Br_F{}^-]$	χ_3
67·53	66·78	76·04	9·26	0·773	7·71	8·49	15·37	6·88	16·78
62·71	61·99	76·70	14·71	1·153	12·40	13·56	25·58	12·02	16·64
57·21	56·53	79·06	22·53	1·634	19·26	20·90	41·03	20·13	16·93
51·45	50·81	77·33	26·52	1·754	23·01	24·77	51·39	26·62	17·01
57·15	56·47	84·64	28·17	2·041	24·09	26·13	51·32	25·19	16·93
45·06	44·49	92·96	48·47	2·854	42·76	45·62	102·56	56·94	16·88
48·71	48·09	98·51	50·42	3·179	44·06	47·24	101·72	54·48	16·82
33·25	32·78	111·61	78·85	3·530	71·79	75·32	204·88	129·56	16·90
35·55	35·07	117·46	82·39	3·922	74·55	78·49	205·09	126·62	16·79
23·70	23·34	114·94	91·60	2·997	85·61	88·60	307·24	218·64	16·78
19·63	19·31	32·24	12·93	0·343	12·59	12·24	51·01	38·42	16·50
15·67	15·39	36·90	21·51	0·460	21·05	20·59	101·96	80·91	16·54
13·71	13·45	42·25	28·80	0·541	28·26	27·72	152·91	124·65	16·53
10·91	10·68	42·16	31·48	0·473	31·01	30·53	203·90	172·89	16·53

TABLE 2. χ_3 *at* 35°. *All concentrations are molal* × 10^3. *Units of* χ_3 *are kg. of solvent mole*$^{-1}$.

$[Br_2^F]$*	$[Br_2^F]$	$[Br_2^T]$	$[Br_2^C]$	$[Br_5^-]$	$[Br_3^-]$	$[Br_C^-]$	$[Br_T^-]$	$[Br_F^-]$	χ_3
27·02	26·62	120·28	93·66	3·032	87·60	90·63	305·79	215·16	15·29
27·04	26·64	120·72	94·08	3·047	87·99	91·03	305·18	214·15	15·42
38·43	37·92	118·16	80·24	3·601	73·04	76·64	203·85	127·21	15·14
37·12	36·62	115·23	78·61	3·417	71·78	75·19	203·73	128·54	15·25
49·05	48·43	96·06	47·63	2·663	42·30	44·97	101·99	57·02	15·32
58·35	57·66	84·14	26·48	1·726	23·03	24·75	51·06	26·31	15·18
58·49	57·80	79·05	21·25	1·388	18·47	19·86	40·79	20·93	15·27
61·27	60·56	82·39	21·83	1·485	18·86	20·34	40·77	20·43	15·24
58·14	57·45	70·75	13·30	0·864	11·57	12·44	25·54	13·10	15·37

TABLE 3. χ_3 *at* 5°. *All concentrations are molal* × 10^3. *Units of* χ_3 *are kg. of solvent mole*$^{-1}$.

$[Br_2^F]$*	$[Br_2^F]$	$[Br_2^T]$	$[Br_2^C]$	$[Br_5^-]$	$[Br_5^-]$	$[Br_C^-]$	$[Br_T^-]$	$[Br_F^-]$	χ_3
23·86	23·72	93·94	70·22	2·958	64·30	67·26	203·82	136·56	19·85
36·07	35·87	106·43	70·56	4·310	61·94	66·25	152·84	86·59	19·94
35·51	35·31	81·67	46·36	2·793	40·77	43·57	102·01	58·44	19·76
51·30	51·05	80·33	29·28	2·420	24·44	26·86	51·02	24·16	19·82
51·13	50·88	80·06	29·18	2·406	24·37	26·77	50·94	24·17	19·82
58·61	58·33	74·20	15·87	1·464	12·94	14·41	25·54	11·13	19·93

subsequent calculations on the equilibria in the mercuric bromide–bromide ion system the value of χ_3 and of $\chi_{3,5}$ appropriate to the range of bromine concentration employed was used. This avoided the difficulty in the only simple manner which was possible.

(ii) At 35°.—The same " hydrolysis correction " was necessary, and the results are displayed in Table 2. From the corrected values a linear plot of α against β was obtained, and, from the slope, a value of $\chi_{3,5} = 1{\cdot}30$ kg. mole^{-1}. The mean of nine separate estimates of χ_3, obtained as described earlier, was 15·28 kg. mole^{-1}, standard deviation of the mean 0·08.

(iii) At 5°.—A lower " hydrolysis constant " of $5{\cdot}9 \times 10^{-9}$ kg.$^{-2}$ mole^2 was required to give a linear plot of α against β, when the data of Table 3 were used. This compares with the value $\chi_h = 0{\cdot}57 \times 10^{-9}$ kg.$^{-2}$ mole^2 found by Jones and Hartmann.[4] From the slope of this plot $\chi_{3,5} = 1{\cdot}94$ kg. mole^{-1}. The six calculated values of χ_3 gave a mean of 19·85 kg. mole^{-1}, standard deviation 0·07.

DISCUSSION

The reproducibility of the results compares favourably with the best previous work. The only extensive series previously reported at constant salt concentration was that due to Griffith, McKeown, and Winn [4] who used a liquid-phase partition method and applied a correction for the activity coefficient of bromine. Six determinations in 0·1 molar potassium bromide over a bromine concentration range 5—46 mmoles l.$^{-1}$ gave a mean $\chi_3 = 17{\cdot}40$ l. mole^{-1}, and a standard deviation of the mean of 0·05 at 21·5°. Over a range of ionic strengths quite large variations in χ_3 have been observed, and there is in addition a small but definite effect due to the cation. For example, Jones and Baeckström [2] used the present method and, after correcting for the change in activity of the bromine, found χ_3 to vary between 15·5 and 19·3 as the potassium bromide content varied between 0·01 and 1·0 molar, and the bromine content from about 0·01 to 0·75 molar. On the whole their values increased with decreasing salt content; this was not found by Griffiths, McKeown, and Winn,[4] who concluded that the constant increased with increasing ionic strength up to $I = 0{\cdot}3$—$0{\cdot}6$, and then decreased again. Jones and Baeckström selected $\chi_3 = 16$ l. mole^{-1}, and $\chi_{3,5} = 2{\cdot}5$ l. mole^{-1} as the " best " values at 25°; these are as close to our present values (which are expressed in terms of molal concentrations) as can reasonably be expected, especially since these refer to solutions in which the ratio of bromine to bromide was higher than that used in either ref. 2 or 4. A selection of earlier values is shown in Table 4, from which the effects of temperature and of the cation used can be seen.

The importance of using χ_3 values obtained under the experimental conditions which are to be used in any subsequent complex studies is clear from inspection of this Table.

TABLE 4. *Selected earlier values of χ_3 (l. mole^{-1}).*

Salt	Temp.	χ_3	Source	Salt	Temp.	χ_3	Source
KBr	0°	19·6	Jones and Hartmann[3]	NaBr ($I = 0{\cdot}5$)	21·5°	16·6	ref. 4
KBr ($I = 0{\cdot}5$)	16·5	18·2	ref. 4	LiBr ($I = 0{\cdot}5$)	21·5	16·2	,,
NaBr ($I = 0{\cdot}5$)	16·5	17·4	,,	KBr	25·0	16·1	ref. 3, calc. by Lewis and Storch[8]
KBr ($I = 0{\cdot}5$)	21·5	17·4 (mean of two)	,,	KBr	32·5	15·4	ref. 1

Thermodynamic constants for the reaction between bromine and a bromide ion to form the tribromide ion when reactants and products are at unit mole fraction can be obtained without serious error from the experimental equilibrium constants (see following paper). $\Delta G_3°$ proves to be almost independent of temperature; at 278° K it is -1650 cal. mole^{-1}, at 298° K, -1670 cal. mole^{-1}, and at 308° K, -1670 cal. mole^{-1} also. Thus the entropy change during the addition of the bromide ion to the bromine molecule is very small (~ 0) and comparable with that for the formation of the tri-iodide ion from iodine and an iodide ion. This can be calculated to be about $-1{\cdot}5$ cal. mole^{-1} deg.$^{-1}$ from Jones and Kaplan's data,[9] who measured χ_3 at 0° and 25°. The possibility of serious error in this kind of calculation is however well shown by comparing this value with the much larger negative one (-5 cal. mole^{-1} deg.$^{-1}$) found in a recent extinctiometric study of the iodine-tri-iodide equilibrium [10] and the above value for $\Delta S_3°$ is not to be regarded as definitive.

SHEFFIELD UNIVERSITY.

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[9] Jones and Kaplan, *J. Amer. Chem. Soc.*, 1928, **50**, 1845.
[10] Awtrey and Connick, *ibid.*, 1951, **73**, 1842.