The Stability Constants of the Indium Halides.

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Stepwise equilibrium in complex solutions of indium halides at 20° has been investigated for halide concentrations up to 0·5M. Radioactive indium was employed in conjunction with a strong cation-exchange resin in the H^+-form, and the ionic strength was maintained at 0·691M with perchloric acid. The existence of the complex species InA^{2+}, InA_2^+, and InA_3 was established ($A = Cl^-$, Br^-, and I^-) and their stability constants, K_j, were measured. The stabilities decreased in the order $Cl > Br > I$, and $K_1 > K_2 > K_3$. Anionic complexes were shown to be considerably weaker.

Studies of the solvent-extraction of indium halides (Irving, Rossotti, and Drysdale, *Nature*, 1952, **169**, 619; Irving and Rossotti, *Analyst*, 1952, **77**, 801) and a growing appreciation of the important part which the stepwise formation of complexes InA_j^{3-j} ($A = Cl$, Br, or I) play in such systems (Irving and Rossotti, unpublished work) made it desirable to obtain values for the individual stability constants defined by $\beta_j = [InA_j^{3-j}]/[In^{3+}][A^-]^j$, ($j = 0, 1, \ldots n$; and $[InA_0^{3+}] = [In^{3+}]$).

Until recently very few investigations of aqueous solutions of indium halides were reported. On the assumption that only the 1 : 1-complexes were formed ($j = 1$), Hepler and Hugus (*J. Amer. Chem. Soc.*, 1952, **74**, 6115) calculated values of β_1 for indium chloride, bromide, and iodide complexes from data reported by Moeller (*ibid.*, 1941, **63**, 1206) on the hydrolysis of different indium salt solutions. A recalculation of the same data here (Rossotti, personal communication) has given substantially smaller values (Table 1). From a polarographic study of the reduction of indium ions in a chloride ion medium Schufle, Stubbs, and Witman (*ibid.*, 1951, **73**, 1013) postulated the existence of the

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* Some aqueous hæmatoxylin solutions, stable in absence of fibre, were found to oxidise in presence of nylon or wool.

complexes $InCl_2^+$ and $InCl_4^-$ and reported values for their stability ($\beta_2 = 30$—67, and $\beta_4 = 0{\cdot}08$—0·17). These figures do not appear to be very reliable owing to variations in the ionic strength and to uncertainties in the standard potentials of the cells. In a more recent and extensive polarographic investigation Cozzi and Vivarelli (*Z. Electrochem.*, 1953, **57**, 408) established the concentration ranges over which the various indium halide complexes predominated, and although actual stability constants were not reported, the order of decreasing stability was clearly shown to be $Cl > Br > I$. While the present work was in progress values for the first three stability constants for all the indium halide systems were obtained by an ion-exchange method by Schufle and Eiland (*J. Amer. Chem. Soc.*, 1954, **76**, 960), and a careful and comprehensive investigation of the complex chemistry of indium, including that of its halides, has been undertaken by Sundén (*Svensk Kem. Tidskr.*, 1953, **65**, 257; 1954, **66**, 20, 50). A summary of the published data, together with values obtained in the present investigation appears in Table 1. Discrepancies will be discussed later (p. 4395).

The method employed in the present investigation differed from that originally developed by Fronaeus (*Acta Chem. Scand.*, 1951, **5**, 859; *Svensk Kem. Tidskr.*, 1953, **65**, 19) and followed by Schufle and Eiland (*loc. cit.*) in that the strong cation-exchange resin was used in the H^+-form rather than in the sodium-ion form. In order to secure a conveniently measurable distribution ratio between the hydrogen ions and tervalent indium ions, which are adsorbed very strongly on the resin, the hydrogen-ion concentration in solution was held constant and fairly high (0·691M) throughout the experiments by the use of perchloric acid. This does not interfere through competitive complex formation, but it ensures that the equilibrations are effected at an acidity where the hydrolysis of the aquated indium ions is completely suppressed. Moreover, on maintainance of a constant ionic strength, the activity coefficients of species in the aqueous phase may be regarded as constant.

TABLE 1.

	Fluoride			Chloride			Bromide			Iodide		
Authors	β_1	β_2	β_3	β_1	β_2	β_3	β_1	β_2	β_3	β_1	β_2	β_3
Hepler and Hugus [a, b]	—	—	—	225	—	—	159	—	—	95·5	—	—
Rossotti [b]	—	—	—	110	—	—	66	—	—	49	—	—
Schufle, Stubbs, and Witman [c]	—	—	—	—	30—67	—	—	—	—	—	—	—
Schufle and Eiland [d]	10^3	6×10^5	4×10^8	26	170	1680	16	60	300	2	—	—
Sundén [e]	—	—	—	140	3900	—	95	360	—	10	180	—
Sundén [f]	5×10^3	18×10^5	4×10^8	—	—	—	—	—	—	—	—	—
Present authors [g] ...	—	—	—	227	4250	8950	103	1250	1900	44	360	300
Present authors [h] ...	6×10^3	26×10^5	—	—	—	—	—	—	—	—	—	—

[a] *J. Amer. Chem. Soc.*, 1952, **74**, 6115. [b] Calc. from data by Moeller (*loc. cit.*) for 25° which refers to pH 1·4—3·3 and ionic strength μ up to 0·04M. [c] *Ibid.*, 1951, **73**, 1013. Data for 25° and $\mu = 0{\cdot}01$—4M and pH —0·6 to 2. [d] *Ibid.*, 1954, **76**, 960. Data for 25° and M-sodium perchlorate at pH 3·8. [e] *Svensk Kem. Tidskr.*, 1954, **66**, 20. Data for 20° and μ = 2M-sodium perchlorate at pH 2—2·6. [f] *Ibid.*, p. 50. Data for 20° and μ = M-sodium perchlorate at pH 2—2·6. [g] Data for 20° and μ = 0·691M-perchloric acid at pH =0·16. [h] Calc. from potentiometric measurements by Hepler, Kury, and Hugus (*J. Phys. Chem.*, 1954, **58**, 26) for μ = 0·5M at 25° and pH 1·3, assuming $[HF]/[H^+][F^-] = 1{\cdot}15 \times 10^3$.

In deriving stability constants from the experimental data Fronaeus's methods were adopted in the main (*loc. cit.*) and his notation will be used with only minor modifications. Let C'_{In}, and C'_A be the total concentration of indium and ligand (halide ion) in the solutions (in moles/l.) before addition of the ion-exchange resin, and C_{In} and C_A their total concentrations in the aqueous solution after equilibration with the resin. $[M]$ represents the equilibrium concentration of a species in aqueous solution and $[M]_R$ the equilibrium concentration in moles/g. (dry weight) of resin. Then,

$$C_{In} = [In^{3+}] + [InA^{2+}] + [InA_2^{+}] + \ldots\ldots$$

$$= [In^{3+}](1 + \sum_{j=1}^{n} \beta_j[A^-]^j)$$

and

$$(C_{In})_R = [In^{3+}]_R + [InA^{2+}]_R + [InA_2^{+}]_R \quad \ldots\ldots \quad (1)$$

We shall also make use of the polynomials defined by :

$$X = 1 + \sum_{j=1}^{n} \beta_j[\mathrm{A}^-]^j, \text{ and } X_j = (X_{j-1} - \beta_{j-1})/[\mathrm{A}^-]\,;\; (X_0 = X)$$

For each of the species InA_j^{3-j} exchanging for hydrogen ions in the resin we can write :

$$\mathrm{InA}_j^{3-j} + (3-j)(\mathrm{H}^+)_\mathrm{R} \rightleftharpoons (3-j)\mathrm{H}^+ + (\mathrm{InA}_j^{3-j})_\mathrm{R}$$

and by applying the law of mass action to these exchange equilibria :

$$\frac{[\mathrm{InA}_j^{3-j}]_\mathrm{R}}{[\mathrm{InA}_j^{3-j}]} = k_j \cdot \frac{[\mathrm{H}^+]_\mathrm{R}^{3-j}}{[\mathrm{H}^+]^{3-j}} = l_j,\ (j = 0, 1, \text{ and } 2) \quad . \quad . \quad . \quad . \quad (2)$$

Here k_j is a function of the four activity coefficients (see p. 4399). But if the load, $(C_\mathrm{In})_\mathrm{R}$, is kept constant and very much smaller than $[\mathrm{H}^+]_\mathrm{R}$, both $[\mathrm{H}^+]_\mathrm{R}$ and the activity coefficients in the resin phase are effectively constant. These conditions were amply satisfied in the present work since $(C_\mathrm{In})_\mathrm{R}$ was made constant at 10^{-3} millimoles/g. of resin which is very small compared with the total exchange capacity which was found to be 4·5 milliequivs./g. of oven-dried resin. Since, further, the actual hydrogen-ion concentration in the aqueous phase was kept constant, as was also the ionic strength (and hence the activity coefficients), both k_j and l_j may be regarded as constant.

The distribution of indium between resin and solution is given by :

$$\phi = (C_\mathrm{In})_\mathrm{R}/C_\mathrm{In} = l_0(1 + l_1'[\mathrm{A}^-] + l_2'[\mathrm{A}^-]^2)/X \quad . \quad . \quad . \quad . \quad (3)$$

using equation (2) and the definitions of β_j and writing $l_j' = l_j\beta_j/l_0$. Now if v is the initial volume of the solution, $v\delta$ the volume at equilibrium (where the factor δ is due to the swelling of the dry resin in contact with solution, cf. Fronaeus, *loc. cit.*), then

$$vC_\mathrm{In}' = v\delta C_\mathrm{In} + m(C_\mathrm{In})_\mathrm{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where m is the mass of the dry resin used. Equation (4) permits the calculation of the load, $(C_\mathrm{In})_\mathrm{R}$, from the experimental values of C_In', C_In, v, m, and δ, and thence the value of ϕ. Since in all experiments $C_\mathrm{In} \ll C_\mathrm{A}$, $[\mathrm{A}^-]$ is obtained with sufficient accuracy from the relationship $[\mathrm{A}^-] \cong C_\mathrm{A} = C_\mathrm{A}'/\delta$. We thus have corresponding values of ϕ and $[\mathrm{A}^-]$ which must satisfy equation (3), and the problem is to determine therefrom the desired unknown stability constants β_j. To facilitate these calculations two new parameters are introduced, *viz.*,

$$\phi_1 = (l_0 \cdot \phi^{-1} - 1)/[\mathrm{A}^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$f = \Big(l_0\phi^{-1}\{(\beta_1 - l_1')[\mathrm{A}^-] - 1\} + 1\Big)/[\mathrm{A}^-]^2 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Introducing the value of ϕ from equation (3) we obtain :

$$\phi_1 = \frac{\beta_1 - l_1' + [\mathrm{A}^-](X_2 - l_2')}{1 + l_1'[\mathrm{A}^-] + l_2'[\mathrm{A}^-]^2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$f = \frac{\beta_1(\beta_1 - l_1') + l_2' - \beta_2 + [\mathrm{A}^-]\{X_2(\beta_1 - l_1') - X_3\}}{1 + l_1'[\mathrm{A}^-] + l_2'[\mathrm{A}^-]^2} \quad . \quad . \quad . \quad . \quad (8)$$

Since $X_j = \sum_{i=j}^{n}\beta_i[\mathrm{A}^-]^{i-j}$ is always a monotonic increasing function of $[\mathrm{A}^-]$. we can write

$$\phi_1{}^0 = \lim_{[\mathrm{A}^-]\to 0} \phi_1 = \beta_1 - l_1' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$f^0 = \lim_{\mathrm{A}^-]\to 0} f = \beta_1(\beta_1 - l_1') - (\beta_2 - l_2') \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The necessary graphical extrapolations can be made with ease as illustrated in Fig. 1. By combining equations (5), (7), and (6), it can be shown that:

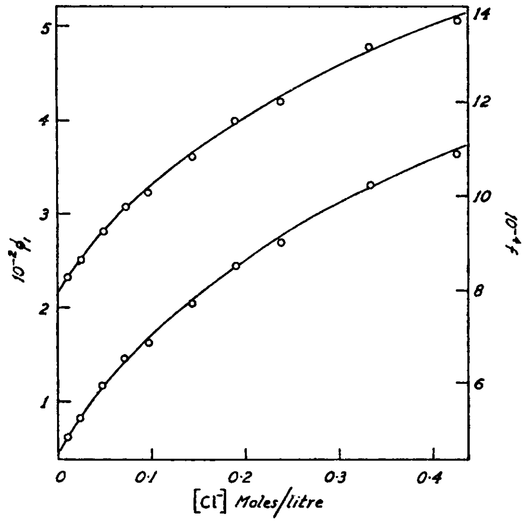
$$f = \beta_1\phi_1 - X_2 + l_2'(\phi_1[A^-] + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Then if $\Delta f = f - f^0$, and $\Delta\phi_1 = \phi_1 - \phi_1{}^0$, we have:

$$\Delta f/[A^-] = \beta_1\Delta\phi_1/[A^-] + l_2'(\phi_1{}^0 + \Delta\phi_1) - \beta_3 - [A^-]X_4 \quad . \quad . \quad . \quad (12)$$

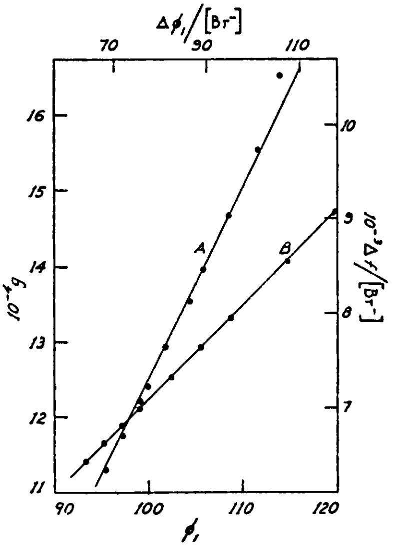
In the present experiments it is found that $[A^-]X_4 \simeq l_2'\Delta\phi_1$. Thus β_1 follows from the slope of the straight line obtained by plotting $\Delta f/[A^-]$ against $\Delta\phi_1/[A^-]$ (cf. Fig 2, curve *A*). However, β_3 cannot be determined accurately without a knowledge of l_2', a point which has been overlooked by Schufle and Eiland (*loc. cit.*) who do not take into account the possibility of $InA_2{}^+$ displacing H^+ from the resin.

FIG. 1. *Evaluation of $\phi_1{}^0$ and f^0 for the indium–chloride ion system.*



Upper curve, ϕ_1;
Lower curve, f.

FIG. 2. *Evaluation of β_1, β_2, and β_3 for the indium–bromide ion system.*



For *A*, see above;
for *B*, $g = \beta_2\phi_1 - X_3$; see below.

Knowing β_1, both l_1' and $(\beta_2 - l_2')$ can now be calculated from equations (9) and (10). Combining equation (11) with equation (5) after adding and subtracting $\beta_2\phi_1[A^-]$ we obtain an equivalent expression for *f*, *viz.*:

$$f = \beta_1\phi_1 + \beta_2\phi_1[A^-] - X_3[A^-] - l_0\phi^{-1}(\beta_2 - l_2') \quad . \quad . \quad . \quad . \quad (13)$$

Introducing a new parameter, we get:

$$g = \beta_2\phi_1 - \beta_3 - X_4[A^-] = \{f - \beta_1\phi_1 + l_0\phi^{-1}(\beta_2 - l_2')\}/[A^-] \quad . \quad . \quad (14)$$

A straight line is obtained from data for each of the three halides when *g* is plotted against ϕ_1 (cf. Fig. 2, curve *B*) showing that the term $X_4[A^-]$ of equation (14) is negligible, *i.e.*, that anionic complexes are not present to any significant extent at the halide concentrations employed. The slope of this plot gives β_2 while the intercept gives β_3 with reasonable accuracy. However, now that β_2 is known, the value of l_2' can be calculated from equation (10) and introduced into equation (11) and the parameter X_2 calculated for various values of $[A^-]$. From the graph of $[A^-]$ against

$$X_2 = \beta_2 + \beta_3[A^-] + \beta_4[A^-]^2 + [A^-]^3X_5$$

points corresponding to the lower values of $[A^-]$ give an excellent straight line of slope β_3 while the intercept confirms the value of β_2 previously adopted. The deviations from linearity at high values of $[A^-]$ only permit of a crude approximation to the value of β_4 owing to the accumulation of uncertainties in the values of the constants already calculated.

All the above equations have been deduced on the assumption that no polynuclear species such as In_2^{6+}, In_2A^{5+} . . . , In_3^{+9}, In_3A^{8+} . . . , $In_mA_n^{3m-n}$ are formed, either in the resin or in solution. Measurements of the extraction of indium into a ketonic solvent from solutions of high bromide-ion concentration (Irving and Rossotti, unpublished work) certainly provide support for the existence of such species as In_2Br_6 and $In_2Br_7^-$. The distribution ratio ϕ was found to vary slightly with the load, $(C_{In})_R$, in the present experiments, confirming Fronaeus's observations, but being contrary to those of Schufle and Eiland. But a consideration of the full sets of equations shows that if polynuclear complexes were formed and were also adsorbed in the resin, the variations expected in ϕ would be in the opposite direction to those actually found. If, on the other hand, polynuclear complexes are assumed to exist only in the solution, the predicted variations in ϕ are certainly in the direction found experimentally; but it is now impossible to calculate reasonable values for the equilibrium constants, $K_{ij} = [In_iA_j^{3i-j}]/[In^{3+}]^i[A^+]^j$ ($i = 2, 3 \ldots$; $j = 0, 1, 2 \ldots$), of the reactions leading to polynuclear complexes. Thus an improbably high value of $K_{20} = 12{,}000$ was calculated where one of less than 10^{-3} might have been expected. It seems reasonable then to conclude that the formation of polynuclear species is negligible under the present conditions of experiment and to ascribe the small variations in ϕ at constant $[A^-]$ to minor variations in activity coefficients, probably mainly in the resin phase. This emphasises the importance of referring all calculations to a constant load $(C_{In})_R$.

EXPERIMENTAL

Only highly pure analytical reagents were used throughout. A small, accurately known weight of "Speckpure" indium metal irradiated in the Harwell pile was dissolved in 4M-perchloric acid containing a little hydrogen peroxide. After all the peroxide had been expelled by heating, a stock solution of ionic strength 0·691M was made up by means of perchloric acid. Tests for traces of Cl^- were carried out from time to time and were always negative. Stock solutions of hydrochloric and hydrobromic acid were prepared, but hydriodic acid was freshly distilled over red phosphorus before use. All solutions were adjusted to 0·691M.

The cation-exchange resin Amberlite IRA-120, 30—50 mesh, was transformed into the H^+-form, dried in an oven at 90°, and stored in a closed bottle to ensure that the water content should remain constant. The exchange capacity was found to be 4·5 milliequivs. per g. of oven-dried resin.

A fixed volume, v, of the solution of indium complexes, made up from varying volumes of stock radioactive indium and stock halogen acid, was mechanically shaken with a fixed dry weight, m, of the resin in a 20 ml. Pyrex test-tube fitted with a ground-in stopper and immersed in a water thermostat at 20·0°. Equilibrium was found to be reached after about 4 hr., but shaking was always carried out for 12 hr. An exact volume 10·00 ml. of the aqueous phase was transferred to a liquid counter (20th Century Electronic, Type G.M.6), shielded in a lead castle, and counted at constant geometry. Corrections were made for background and dead-time, but none was found necessary for differences in absorption of radiation due to the slightly varied nuclear species in the solution. The number of counts was always high enough to get ½% standard deviation or better. In view of the comparatively short half-life of ^{114}In (49 days) a calibration curve of (corrected) counts per minute against indium concentration was made up freshly every second day from a set of standard reference solutions of known indium concentration: it was always found to be a straight line. Owing to the high acidity of the solutions no adsorption of activity on the walls of the liquid-counter or of the stoppered test-tubes was ever detected.

The swelling factor δ was determined by shaking v ml. of standard halogen acid with m grams of resin and determining the change in hydrogen-ion concentration after equilibration. The value was always found to be 0·97. Since $v = 15$ ml. and $m = 0{\cdot}5$ g. throughout the experiments, the ratio $v/m = 30{\cdot}00$ ml./g. was constant, so the load could readily be calculated from equation (4) in the form $(C_{\text{In}})_{\text{R}} = 30(C_{\text{In}}' - 0{\cdot}97C_{\text{In}})$. As mentioned above, ϕ increases slightly as $(C_{\text{In}})_{\text{R}}$ decreases. The distribution was therefore calculated for the constant value $(C_{\text{In}})_{\text{R}} = 1{\cdot}00 \times 10^{-6}$ mole/g. from three different determinations of ϕ at constant halide ion concentration but varying $(C_{\text{In}})_{\text{R}}$. The graphical interpolations or extrapolations are quite reliable, as the three experimental points are almost collinear.

Special precautions had to be taken when investigating the indium–iodide ion equilibria, since the iodide ions are rapidly oxidised to iodine in acid solution, this reaction being accelerated by light and by radioactive radiation, although the latter is unlikely to be significant at the level of activity employed here. It was found possible to reduce such oxidation to almost negligible proportions by using freshly redistilled hydriodic acid quickly diluted for use with boiled-out distilled water and kept below an atmosphere of nitrogen. The same inert atmosphere was also maintained in the test-tubes during equilibration which was carried out entirely in darkness. Even so it was impossible to avoid a slight oxidation, the extent of which was determined and allowed for in the calculations by measuring the iodine concentration immediately before counting by an absorptiometric method which was occasionally checked volumetrically.

DISCUSSION

The experimental results, and the functions used in evaluating stability and other constants are given in Tables 2 and 3. Figs. 1 and 2 indicate the reliability which can be

TABLE 2.

10^3[A⁻] (moles/l.)	$10^5C'_{\text{In}}$ (moles/l.)	$10^6(C_{\text{In}})_{\text{R}}$ (moles/g.)	$10^3\phi$ (l./g.)	$10^5C'_{\text{In}}$ (moles/l.)	$10^6(C_{\text{In}})_{\text{R}}$ (moles/g.)	$10^3\phi$ (l./g.)	$10^5C'_{\text{In}}$ (moles/l.)	$10^6(C_{\text{In}})_{\text{R}}$ (moles/g.)	$10^3\phi$ (l./g.)
				Chloride system					
	1.			2.			3.		
9·49	3·181	0·850	231	6·35	1·68	226	12·69	3·34	216
23·72	3·116	0·737	108	6·21	1·45	104	12·43	2·86	96
47·45	3·009	0·584	53·2	6·00	1·13	51·0	12·00	2·24	46·0
71·17	2·902	0·464	33·2	5·78	0·915	32·4	11·57	1·78	30·6
94·90	2·794	0·379	24·1	5·57	0·750	23·7	11·15	1·47	22·9
142·35	2·579	0·260	14·7	5·15	0·520	14·5	10·29	1·01	14·1
189·80	2·364	0·179	9·85	4·72	0·360	9·80	9·43	0·72	9·70
237:25	2·149	0·132	7·50	4·29	0·263	7·48	8·57	0·52	7·40
332·16	1·719	0·072	4·75	3·43	0·142	4·75	6·85	0·280	4·70
427·04	1·290	0·043	3·55	2·57	0·082	3·55	5·14	0·161	3·50
				Bromide system					
	1			2.			3.		
0	3·224	0·93	741	6·73	1·95	732	13·46	3·88	715
9·49	3·181	0·89	397	6·64	1·86	388	13·28	3·71	372
23·72	3·116	0·832	231·5	6·56	1·77	227	13·01	3·44	220
47·45	3·009	0·745	135·5	6·28	1·53	131·5	12·56	3·05	124
71·17	2·902	0·671	95·0	6·05	1·38	92·0	12·11	2·72	86·5
94·90	2·794	0·600	72·4	5·83	1·25	70·5	11·67	2·48	67·0
142·35	2·579	0·487	48·5	5·38	1·01	47·4	10·77	1·97	46·0
189·80	2·364	0·395	35·8	4·93	0·815	35·4	9·87	1·60	34·5
237·25	2·149	0·318	28·1	4·49	0·668	27·9	8·98	1·315	27·4
332·16	1·719	0·206	19·30	3·59	0·428	19·20	7·18	0·850	18·95
427·04	1·290	0·128	14·25	2·69	0·265	14·20	5·38	0·522	14·20

Iodide system

	1.				2.				3.		
10^3[A⁻]	$10^5C'_{\text{In}}$	$10^6(C_{\text{In}})_{\text{R}}$	$10^3\phi$	10^3[A⁻]	$10^5C'_{\text{In}}$	$10^6(C_{\text{In}})_{\text{R}}$	$10^3\phi$	10^3[A⁻]	$10^5C'_{\text{In}}$	$10^6(C_{\text{In}})_{\text{R}}$	$10^3\phi$
9·47	3·181	0·907	555	9·44	7·03	2·00	543	9·45	14·06	3·99	525
23·68	3·116	0·873	402	23·65	6·89	1·94	391	23·65	13·77	3·84	376
47·25	3·009	0·815	275	47·22	6·65	1·80	266	47·23	13·30	3·58	255
70·92	2·902	0·770	208	70·95	6·41	1·68	202	70·92	12·82	3·35	193
94·68	2·794	0·715	166·5	94·60	6·17	1·57	162	94·65	12·35	3·12	154·5
142·15	2·579	0·623	118·8	142·1	5·70	1·38	115·5	142·1	11·40	2·74	111
189·3	2·364	0·542	92·0	189·2	5·23	1·18	90·5	189·5	10·45	2·34	88
236·9	2·149	0·460	74·9	236·8	4·75	1·025	74·0	236·95	9·50	2·04	72·2
331·8	1·719	0·336	54·1	331·7	3·80	0·750	53·8	331·8	7·60	1·41	53·5
426·8	1·290	0·234	42·8	426·6	2·85	0·508	42·4	426·75	5·70	1·01	42·0

TABLE 3.

$(C_{\mathrm{In}})_{\mathrm{R}} = 1·00 \times 10^{-6}$ mole/g. of resin.

$10^3[\mathrm{A}^-]$ (moles/l.)	$10^3\phi$ (l./g.)	ϕ_1 (moles/l.)$^{-1}$	$10^{-2}f$ (moles/l.)$^{-2}$	$\Delta\phi_1/[\mathrm{A}^-]$ (moles/l.)$^{-2}$	$10^{-2}\Delta f/[\mathrm{A}^-]$ (moles/l.)$^{-3}$	$10^{-2}g$ (moles/l.)$^{-2}$	X_2 (moles/l.)$^{-2}$
			Chloride system				
0	740	(216)	(448·0)	—	—	—	—
9·49	230	233·6	486·1	1854	4015	9,694	4446
23·72	106·5	250·8	527·0	1467	3331	10,615	4286
47·45	51·5	281·7	594·7	1385	3092	11,870	4595
71·17	32·3	307·8	652·1	1290	2868	12,970	4843
94·90	23·4	322·7	685·8	1124	2506	13,610	4923
142·35	14·1	361·7	771·0	1024	2269	15,170	5430
189·80	9·65	398·6	851·7	962·1	2127	16,820	5923
237·25	7·35	420·1	898·9	860·3	1900	17,730	6275
322·16	4·65	476·1	1021·4	783·0	1726	20,100	7203
427·04	3·40	507·3	1089·5	682·1	1502	21,420	7951
			Bromide system				
0	740	(90·8)	(81·3)	—	—	—	—
9·49	395·5	91·8	82·3	105·4	105·4	1126	1256
23·72	230·5	93·2	83·61	101·18	97·39	1141	1283
47·45	134	95·3	85·59	94·84	90·41	1166	1327
71·17	93·5	97·1	87·32	89·22	84·59	1189	1371
94·90	71·2	99·0	89·01	86·41	81·24	1211	1420
142·35	47·5	102·4	92·18	81·50	76·43	1254	1510
189·80	35·2	105·5	95·01	77·45	72·23	1292	1607
237·25	27·6	108·8	98·03	75·87	70·52	1332	1709
332·16	18·9	114·8	103·57	72·25	67·05	1407	1910
427·04	14·15	120·1	108·38	68·61	63·41	1472	2119
			Iodide system				
0	740	(35·2)	(12·10)	—	—	—	—
9·45	554	35·52	12·15	33·86	5·29	115·9	375
23·65	401	35·75	12·35	23·26	10·57	127·3	369
47·23	273	36·20	12·53	21·17	9·104	128·5	377
70·92	206	36·55	12·67	19·04	8·037	129·7	384
94·65	165	36·82	12·77	17·12	7·079	130·5	393
142·1	117·5	37·24	12·96	14·36	6·052	132·2	408
189·5	91·0	37·63	13·12	12·82	5·383	133·6	420
236·95	74·0	37·98	13·25	11·73	4·853	134·8	435
331·8	53·7	38·52	13·46	10·01	4·099	136·8	465
426·75	42·0	38·94	13·62	8·76	3·562	138·3	494

TABLE 4. *Stability constants valid for* 20° *and* 0·691M-*perchloric acid.*

	β_1	β_2	β_3	K_1	K_2	K_3
Chloride	227 ± 4	4250 ± 800	8950 ± 3000	227	18·7	2·1
Bromide	103 ± 3	1250 ± 300	1900 ± 700	103	12·1	1·5
Iodide	44 ± 5	360 ± 175	300 ± 150	44	8·2	0·8

placed on the various graphical procedures. Table 4 summarises values derived in the present work for overall stability constants, β_j, as well as for the step-constants $K_j = \beta_j/\beta_{j-1}$.

From the summary, provided by Table 1, it will be obvious that values reported by Schufle *et al.* disagree with those of other workers. So far as their ion-exchange measurements are concerned this may partly be due to their use of over-simplified equations and to uncertainties in extrapolations to zero halide-ion concentrations. A more evident weakness is their use of too high a pH which will favour the hydrolysis of the aquated indium ion ($K_{\mathrm{H}} \cong 1·4 \times 10^{-4}$), an effect which will become serious at low halide-ion concentrations. The possibility of competitive hydroxyl-ion complexing leading to the formation of mixed complexes, *e.g.*, $\mathrm{In(OH)A^+}$ as well as $\mathrm{InA_2^+}$, cannot be overlooked and will be especially significant in computing β_2. From the stability constants $[\mathrm{Sn(OH)A}]/[\mathrm{SnOH^+}][\mathrm{A^-}]$, $[\mathrm{SnOH^+}][\mathrm{H^+}]/[\mathrm{Sn^{++}}]$, and $[\mathrm{SnA_2}]/[\mathrm{Sn^{++}}][\mathrm{A^-}]^2$, where $\mathrm{A = Cl^-}$ or $\mathrm{Br^-}$, given by Vanderzee and Rhodes (*J. Amer. Chem. Soc.*, 1952, **74**, 3552, 4806) we can calculate $[\mathrm{Sn(OH)A}]/[\mathrm{SnA_2}] \cong 4 \times 10^{-3}/[\mathrm{H^+}][\mathrm{A^-}]$. In these systems with $[\mathrm{A^-}] = 0·1$M or less, the co-ordination of $\mathrm{OH^-}$ to the 1 : 1 complex $\mathrm{SnA^+}$ will predominate over that of $\mathrm{A^-}$ unless the pH is below 1·4; with $[\mathrm{A^-}]$ at 0·01M the pH must lie below 0·4. While comparable figures are not available for indium, the possibility that $In(OH)A^+$ is of greater significance than InA_2^+ in interpreting data on the hydrolysis of indium halides has already been advanced by Hepler and Hugus (*loc. cit.*).

Changes in ionic strength will naturally affect the values measured for stability constants. For the system Cd^{++}–Cl^- which has been most carefully studied (Vanderzee, *ibid.*, 1953, **75**, 5659) minimum values occur round about $\mu = 1$ with a slight rise in stability in higher salt concentrations and a very steep rise in stability as zero ionic

TABLE 5.

	Fluorides		Chlorides		Bromides		Iodides	
Metal	K_1	K_1/K_2	K_1	K_1/K_2	K_1	K_1/K_2	K_1	K_1/K_2
Zn^{++}	—	—	0·63	1·6[a]	0·25[a]	—	<0·05[a]	—
Cu^{++}	—	—	0·63	3·2[b]	0·4	1·6[c]	—	—
			1·30	5·6[d]				
			1·1[e]		0·94[f]			
Sn^{++}	—	—	14	3·9[g]	5·4	2·1[h]	—	—
UO_2^{++}	3·9 × 10^4	18[i]	0·8[j]	—	0·5[j]	—	—	—
Al^{3+}	13·6 × 10^5	13·1[k]	—	—	—	—	—	—
Fe^{3+}	1·42 × 10^5	14[l]	4·2	3·2[n]	0·5[n]	—	—	—
	*1·9 × 10^5	18[m]	30	6·7[p]				
			5·7	2·8[q]				
Ga^{3+}	*1·2 × 10^5[r]	—	—	—	—	—	—	—
Cr^{3+}	*2·6 × 10^4[r]	10	—	—	—	—	—	—
In^{3+}	5 × 10^3	14[s]	140	5[s]	95	25[s]	10	0·55[s]
			227	12[t]	103	8·6[t]	44	5·4[t]
	1 × 10^3	1·7[u]	26	4[u]	16	4·3[u]	2[v]	—
Ce^{3+}	10^4[v]	—	3[v]	—	2·4[v]	—	~0[u]	—
Tl^{3+}	—	—	1·3 × 10^3	398[w]	5·0 × 10^9	620[w]	—	—
Th^{4+}	*4·5 × 10^7	69[l, m]	—	—	—	—	—	—
	*5·0 × 10^7	86[x]	1·3	13·5[x]	—	—	—	—
Zr^{4+}	*6·3 × 10^8	30[y]	—	—	—	—	—	—
U^{4+}	—	—	2[x]	—	1·5[z]	—	—	—
Cd^{++}	2·9	2·5[aa]	38·5	8·8[bb]	57	14·8[bb]	120	29[bb]
			22·3	8·3[cc]				
Hg^{++}	$K_1K_2<10^3$[kk]	—	5·5 × 10^6	1·8[dd]	1·1 × 10^9	6[ee]	7·3 × 10^{12}	81[ff]
Cu^+	—	—	3·2 × 10^6	4·8 × 10^7[gg]	1·6 × 10^8	2·6 × 10^7[gg]	9·1 × 10^{11}	5·7 × 10^8
Ag^+	0·48[hh]	—	1·1 × 10^3	11[ii]	2·4 × 10^4	26[jj]	$K_1K_2 \cong 10^{14}$[ll]	—

[a] Sillén and Liljeqvist, *Svensk Kem. Tidskr.*, 1944, **56**, 85; 25° and $\mu = 3·0$. [b] Bjerrum, *Kgl. Danske Videnskab. Selsk.*, *Mat.-fys. Medd.*, 1946, **22**, No. 18; 23° and various ionic strengths. [c] Näsänen and Lumme, *Acta Chem. Scand.*, 1951, **5**, 13; 25°, $\mu = 1$. [d] McConnell and Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 3164; 25·2° and $\mu = 1$. [e] Näsänen, *Acta Chem. Scand.*, 1950, **4**, 140; 25°, $\mu = 0$. [f] *Idem*, *ibid.*, p. 816; 25°, $\mu = 0$. [g] Vanderzee and Rhodes, *J. Amer. Chem. Soc.*, 1952, **74**, 3552; 25° and $\mu = 3·0$. [h] Vanderzee, *ibid.*, p. 4806; 25° and $\mu = 3·0$. [i] Ahrland and Larsson, *Acta Chem. Scand.*, 1954, **8**, 354; 20° and $\mu = 1·0$. [j] Ahrland, *ibid.*, 1951, **5**, 1271; 20° and $\mu = 1$. [k] Brosset and Orring, *Svensk Kem. Tidskr.*, 1943, **55**, 101; 0·53M-KNO_3. [l] Brosset and Gustaver, *ibid.*, 1942, **54**, 185; 0·53M-KNO_3. [m] Dodgen and Rollefson, *J. Amer. Chem. Soc.*, 1949, **71**, 2600; 25° and $\mu = 0·5$. [n] Rabinowitch and Stockmayer, *ibid.*, 1942, **64**, 335; 26·7° and $\mu = 1$. [p] *Idem*, *loc. cit.*; 25° and $\mu = 0$. [q] Olerup, *Svensk Kem. Tidskr.*, 1943, **55**, 324; 20° and $\mu = 2$. [r] Wilson and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 3509; 25° and $\mu = 0·5$. [s] Sundén, *locc. cit.* [t] Present authors. [u] Schufle *et al.*, *locc. cit.* [v] Mayer and Schwartz, *J. Amer. Chem. Soc.*, 1951, **73**, 222; fluoride at $\mu = 0·5$; chloride in 0·6M-hydrochloric acid; bromide in 0·5—1·7M-sodium bromide; iodide in 0·5M-sodium iodide. [w] Benoit, *Bull. Soc. chim.*, 1949, 518; 18° and $\mu = 0·1$. [x] Zebrowski, Alter, and Heumann, *J. Amer. Chem. Soc.*, 1951, **73**, 5646; $\mu = 0·5$. [y] Connick and McVey, *ibid.*, 1949, **71**, 3182; $\mu = 2$. [z] Ahrland and Larsson, *Acta Chem. Scand.*, 1954, **8**, 137. [aa] Leden, Thesis, Lund 1943, p. 48; 25° and $\mu = 1$. [bb] Leden, *Z. physikal. Chem.*, 1941, **188**, *A*, 160; 25° and $\mu = 3$. [cc] Vanderzee and Dawson, *J. Amer. Chem. Soc.*, 1953, **75**, 5659; 25° and $\mu = 1$. This paper gives data for 0° and 45° also at five ionic strengths up to 3M. [dd] Lindgren, Jonsson, and Sillén, *Acta Chem. Scand.*, 1947, **1**, 479; 25° and $\mu = 0·5$. [ee] Bethge, Jonewall-Westöö, and Sillén, *ibid.*, 1948, **2**, 828; 25° and $\mu = 0·5$. [ff] Qvarfort and Sillén, *ibid.*, 1949, **3**, 505; 25° and $\mu = 0·5$. [gg] Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," 2nd Ed., N.Y., 1952, p. 186. [hh] Leden and Marslin, *Acta Chem. Scand.*, 1952, **6**, 1125; 25° and $\mu = 1$. [ii] Berne and Leden, *Svensk Kem. Tidskr.*, 1953, **65**, 88; 25° and $\mu = 0$; values at $\mu = 0·2$ and 5M are also given. [jj] Berne and Leden, *Z. Naturforsch.*, 1953, **8a**, 719; same conditions. [kk] Bjerrum, *Chem. Reviews*, 1950, **46**, 381. [ll] Rough estimation from data of Bódländer and Eberlein, *Z. anorg. Chem.*, 1904, **39**, 197; Erber, *ibid.*, 1941, **248**, 36; cf. Makor, *Rec. Trav. chim.*, 1951, **70**, 457. Further data for fluoride complexes are collected by McKay, A.E.R.E. Report C/R 884. * refers to values calculated from data in the literature quoted by using $[HF]/[H^+][F^-] = 10^3$. Variation in ionic strength can make appreciable differences in the values of K_1 and K_2 (cf. refs. *cc* and *ii*). Although too much emphasis must not be placed on the absolute values of stability constants when comparing one element with another, especially when the ionic strength is appreciably different, the trend of values discussed in the text is not in doubt.

strength is approached. The uniformly much lower stability constants reported by Schufle *et al.* for all halide systems can therefore scarcely be due to differences in ionic strength, and they persist in the fluoride system (Table 1) where measurements at the same ionic strength ($\mu = 1$) can be compared.

Divergencies between the present results and those of Sundén are not readily explicable but are not large considering the differences in salt background. Although Sundén employed less acid solutions than here, he showed experimentally that hydrolysis of the indium ions could be neglected under his conditions. His values for the fluoride system agree excellently with those calculated from potentiometric data of Hepler, Kury, and Hugus (*J. Phys. Chem.*, 1954, **58**, 26), derived from changes in the redox potential Fe^{2+}/Fe^{3+} in the presence of fluoride and indium ions. On the other hand we are inclined to discount Sundén's values for the iodide system (or at least his value for β_1) and several of Schufle's values on the following grounds.

Stability constants quoted in the accompanying Table 5 show that halides fall into two distinct groups. (i) Cuprous copper, silver, cadmium, and mercury (and probably thallic ions) form fluoride complexes of very low stability, those with the other halogens increasing in the order F < Cl < Br < I. Invariably $K_1 > K_2$, and the actual magnitude of the stability constants is often very high indeed, approaching values found for ammines and chelates of the transition metals (cf. Irving and Williams, *J.*, 1953, 3192). It is noteworthy that the ratio K_1/K_2 increases in the order Cl < Br < I, *i.e.*, in the order of increasing stability of the complexes. (ii) All other metal halides so far examined show stabilities which decrease in the order F > Cl > Br > I. Where they have been studied the stabilities of the fluoride complexes are very high compared with those of the other halides. Here again invariably $K_1 > K_2$, but the ratio K_1/K_2 decreases in the order Cl > Br > I, *i.e.*, it again follows the order of stability of the halides.

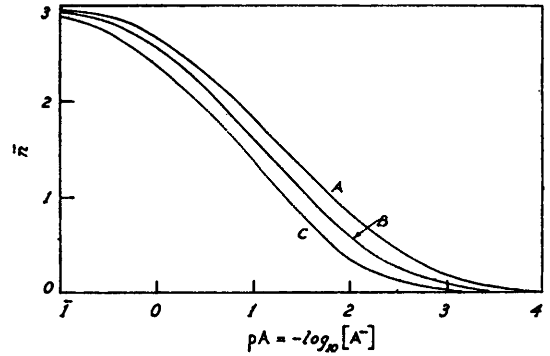


FIG. 3. *Formation curves for indium halide complexes.*
A, Chloride; *B*, bromide; *C*, iodide.

Indium is exceptional in that it is the only element apart from cadmium for which it has proved possible to study all the halides and to obtain values for the stability of more than one step-complex in each system. It clearly takes its place among the halides of type (ii), though there is evidence of transitional character. Thus in the vertical series Zn, Cd, Hg there is not only a change from type (ii) to type (i), but there is a striking increase in the magnitude of the stability constants, with Cd holding an intermediate position. For reasons connected with the redox potential of the Tl^{3+}/Tl^{+} couple it is impossible to study the complexity of thallic iodide, but Benoit's figures for thallic chloride and bromide complexes show that the complexity is outstandingly high and increases Cl < Br. If, as seems probable, thallium is to be classified among type (i) halides, the stability of its fluoride will be low. By extrapolation of the empirical relation log K = 2·24 − 13 log (ionic radius), which we find holds quite well for aluminium, iron, gallium, and indium, a value of $K_1 \cong 200$ would be predicted.

One fact is established by Table 5. In every case $K_1 > K_2$. Support for this comes from measurements of acetate, thiocyanate, and sulphate complexes made by Sillén, Fronaeus, Ahrland, and others. It holds for all types of ligands and cations save where orbital stabilisation can take place. The one exception now known is in the dipyridyl and 1 : 10-phenanthroline complexes of ferrous iron (Irving and Williams, *loc. cit.*). It therefore appears that Sundén's figures for the indium iodide complexes, for which he reports $K_1 = 10$, but $K_2 = 18$, must be in error. Further, whereas the " normal " trend for the ratio K_1/K_2 to decrease in the order Cl > Br > I appears in the present measurements (12, 8·6, and 5·4 respectively), Sundén's ratio for the bromide system (25) is greater than his value for the chloride system (5) and it seems probable that his value of β_2 for the bromide system is too low.

For all halides of type (ii), as well as for acetate, thiocyanate, and sulphate complexes, $K_2/K_3 = >1$. By this test Schufle's β_3 for the chloride system appears to be improbably high while the values for the fluoride and bromide systems may also be overestimated.

With the concentrations in the resin phase expressed in the customary manner (mole fractions) and denoting activity coefficients in solution by γ, the exchange constants of equation (2) are related to thermodynamic values by the expression :

$$k_j{}^{\mathrm{T}} = l_j(\gamma_{\mathrm{H}^+} \,.\, [\mathrm{H}^+])^{3-j}/\{\gamma_{\mathrm{InA}_j{}^{3-j}} \,.\, [\mathrm{H}^+]_{\mathrm{R}}\}\,;\ j = 0,\ 1,\ \text{and}\ 2$$

provided the condition $(C_{\mathrm{In}})_{\mathrm{R}} \ll (\mathrm{H}^+)_{\mathrm{R}}$ is valid, for then the activity coefficients in the resin phase may be regarded as almost constant and equal to unity. The activity coefficients in solution may be computed from Harned and Owen's tables (" The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Co., New York, 1950) and hence values of $k_j{}^{\mathrm{T}}$ determined. These are expressed in Table 6 in relation to a resin in the sodium ion form, the transformation being carried out by means of the known exchange constant, $k_0{}^{\mathrm{T}} = 1{\cdot}24$, for the reaction $\mathrm{Na}^+ + (\mathrm{H}^+)_{\mathrm{R}} \rightleftharpoons (\mathrm{Na}^+)_{\mathrm{R}} + \mathrm{H}^+$. Constants calculated in the same way from measurements by Fronaeus, and by Schufle and Eiland (*locc. cit.*) are included for comparison. It appears that In^{3+} is less strongly adsorbed than Ce^{3+}. The trends in the adsorbabilities of the complex ions are what would be expected from their size and charges, though the low value for $\mathrm{InCl_2}^+$ is surprising and seems to indicate that the ionic radius of hydrated $\mathrm{InCl_2}^+$ is larger than that of hydrated H^+.

TABLE 6.

Author	System	l_0 (l./g.)	$10^2 l_1$ (l./g.)	$10^3 l_2$ (l./g.)	$k_0{}^{\mathrm{T}}$	$k_1{}^{\mathrm{T}}$	$k_2{}^{\mathrm{T}}$	$10^6(C_{\mathrm{M}})_{\mathrm{R}}$ (moles/g.)
Fronaeus	Ce^{3+}–Ac^-	0·68	7·1	9·1	70	12	2·4	30
Schufle *et al.* ...	In^{3+}–Cl^-	0·11	2·1	—	13	3·5	—	~1
,, ...	–Br^-	—	2·3	—	—	3·9	—	,,
,, ...	–I^-	—	4·4	—	—	7·4	—	,,
Carleson	In^{3+}–Cl^-	0·74	3·6	1·4	28	2·5	0·2	1
,, ...	–Br^-	—	8·6	6·6	—	5·9	0·8	,,
,, ...	–I^-	—	15·4	14·2	—	10·4	2·0	,,

Values of l_0 and $k_0{}^{\mathrm{T}}$ refer to pure perchlorate solutions. Those for the other constants are limiting values which refer to perchlorate solutions in which the concentration of other anions approaches zero.

The general similarity between the three complex indium halide systems is displayed in Fig. 3 where the degree of formation (ligand number) defined by $\bar{n} = (C_{\mathrm{A}} - [\mathrm{A}^-])/C_{\mathrm{In}}$ and calculated from the stability constants given in Table 4 is plotted against the free ligand exponent, $\mathrm{pA} = -\log_{10}[\mathrm{A}^-]$.

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