

*The Extraction of Indium at Tracer Concentrations from Acid-Bromide Solutions into isoButyl Methyl Ketone.\**

By H. IRVING and F. J. C. ROSSOTTI.

[Reprint Order No. 5843.]

A detailed study has been made of partition equilibria in the system indium-hydrobromic acid-*isobutyl methyl ketone*,  $^{114}\text{In}$  being used as a tracer. At low metal concentrations (less than  $10^{-5}\text{M}$ ) only mononuclear species exist in the two phases. The acido-complex  $\text{HInBr}_4\text{,aq.}$  predominates in the organic phase at relatively high acidities, but other species such as  $\text{InBr}_3$  and (in the presence of alkali-metal cations) salts or ion-pairs of the type  $\text{A}^+\text{InBr}_4^-$  partition to a lesser extent. At high bromide-ion concentrations the partition of indium still favours the organic phase even when the hydrogen-ion concentration is low. Estimates have been made of the order of magnitude of relevant partition coefficients and equilibrium constants.

THE precise nature of the species which passes on partition into the organic phase has seldom been established with certainty in the solvent extraction of inorganic salts. In some cases its composition has been determined by analysis on the macro-scale, though this provides no direct evidence of molecular complexity and may be misleading if a considerable amount of acid is co-extracted (cf., *inter al.*, Myers, Metzler, and Swift, *J. Amer. Chem. Soc.*, 1950, **72**, 3767; Nachtrieb and Fryxell, *ibid.*, 1949, **71**, 4035; Bock, *Z. anal. Chem.*, 1951, **133**, 110; Bock, Kusche, and Bock, *ibid.*, 1953, **138**, 167). At best, such analyses indicate only the bulk composition of the solute without distinguishing between a single compound and a mixture of several in approximately constant proportions.

In the present paper attempts are made to ascertain the nature of the extracted species in a particular system by detailed studies of partition equilibria. This approach has proved successful with inner complexes derived from the comparatively weakly acidic reagents 8-hydroxyquinoline (oxine) and cupferron (Dyrssen, *Svensk Kem. Tidskr.*, 1953, **65**, 43), dithizone (Irving, Bell, and Williams, *J.*, 1952, 356), or  $\beta$ -diketones (Connick and McVey, *J. Amer. Chem. Soc.*, 1949, **71**, 3182; Rydberg, *Acta Chem. Scand.*, 1950, **4**, 1503). Its extension to the extraction of inorganic species derived from anions of strong acids has been discussed in a previous general paper (Part I\*). However, strict application of the equations deduced therein is limited to systems in which the solvent properties of the two phases do not alter with variations in the concentrations of any of the solutes, so that the constancy of partition coefficients and stability constants may be assumed.

The extraction of indium from a halogen acid offers possibilities for detailed studies, for it appears that the same type of substance is extracted by a wide variety of solvents (Part V\*). However, measurements with hydrochloric acid are unsuitable since they demand high acidities if substantial amounts of indium are to be extracted. In these circumstances the magnitude of the distribution ratio,  $q$ , varies as a high power of the concentration of acid. This cannot be readily explained on the basis of the equations previously deduced (Part I), and the assumption that activities may be replaced by concentrations must break down in hydrochloric acid of the strength needed for extraction owing to the rapid increase of activity with concentration (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, 1950). Indeed, the solution of hydrogen chloride in the aqueous phase brings about a substantial decrease in dielectric constant (Hasted, Ritson, and Collie, *J. Chem. Phys.*, 1948, **16**, 1) which will modify both the stability constants and the partition coefficients of all the dissolved species. Hydriodic acid is also unsuitable for the present purpose since its oxidation during the period of equilibration leads to uncertainties in the required concentrations of free hydrogen and of free iodide ions. The system *isobutyl methyl ketone*-

\* This forms Part III of a group of papers of which Parts I and II are the preceding papers and Parts IV and V are the following papers.

hydrobromic acid was finally selected for detailed study, the choice of solvent resting upon its ability to extract indium to a considerable extent from acid concentrations less than molar, while, over the whole range of concentrations employed, changes in the mutual solubility of the two phases were negligible.

A full investigation of the system would require measurements of the distribution ratio

$$q = \frac{C_o}{C_w} = \frac{\text{Total concentration of indium in the organic phase}}{\text{Total concentration of indium in the aqueous phase}} \quad (1)$$

for the three cases where (i) the concentration of free indium ions,  $[\text{In}^{3+}]$ , is varied while the concentrations of free hydrogen ions,  $[\text{H}^+]$ , and of free bromide ions,  $[\text{Br}^-]$ , are held constant, (ii)  $[\text{H}^+]$  is varied while  $[\text{In}^{3+}]$  and  $[\text{Br}^-]$  are both held constant, and (iii)  $[\text{Br}^-]$  is varied while both  $[\text{In}^{3+}]$  and  $[\text{H}^+]$  are fixed. A useful check on deductions made from (ii) and (iii) can be carried out by varying the total concentration of halogen acid  $C_{\text{HBr}}$ , while  $[\text{In}^{3+}]$  is held constant. By using  $^{114}\text{In}$  in tracer quantities it is possible to keep the total concentration of this metal,  $C_M$ , very much smaller than the total concentrations of either hydrogen ion,  $C_H$ , or of bromide ion,  $C_{\text{Br}}$ . In these circumstances  $[\text{H}^+] \approx C_H$ , and  $[\text{Br}^-] \approx C_{\text{Br}}$ . There is, unfortunately, no way of ensuring the constancy of free indium ions, so that experiments based on procedures (ii) and (iii) can only be interpreted unequivocally where the results satisfy certain theoretical conditions, *viz.*, of being independent of  $[\text{In}^{3+}]$ . In the present work this difficulty was overcome by holding the total concentration of indium in the system constant at a value where measurements of distribution ratios by procedure (i) had proved them to be independent of  $C_M$  and hence of  $[\text{In}^{3+}]$ .

#### EXPERIMENTAL

**Materials.**—Radioactive indium ( $^{114}\text{In}$ ; half-life 49 days) was obtained by irradiation to saturation of a known weight of "Specpure" indium wire (Johnson Matthey, Ltd.) in the nuclear reactor at A.E.R.E., Harwell. The irradiated wire was dissolved by first treating it with cold 5*N*-hydrobromic acid, gentle heat being applied after the initial vigorous reaction had abated. In some cases grey or red insoluble material was formed in the most concentrated solutions but, since clear colourless solutions were always obtained on further warming after the addition of a little hydrogen peroxide, such precipitates may have been due to bromides of a lower valency state of indium, or of a mixed valency state (cf.  $\text{TlBr}_2 \equiv \text{Tl}[\text{TlBr}_4]$ , and  $\text{Tl}_2\text{Br}_3 = \text{Tl}_3\text{TlBr}_6$ ). A stock solution of  $2.5 \times 10^{-2}\text{M}$ -indium in *n*-hydrobromic acid was made by quantitative dilution.

*iso*Butyl methyl ketone was distilled over potassium hydroxide and the fraction of b. p. range 114–116° was collected for use in the distribution experiments. Anhydrous sodium perchlorate was prepared by recrystallising an aqueous solution of the commercial hydrate at 90° and drying to constant weight at 115° (Fronaeus, "Komplexsystem Hos Koppa," Carl Bloms, Lund, 1948, p. 31). After two recrystallisations it was shown to be completely free from chloride and chlorate ions. Pure sodium bromide was available, and hydrobromic acid (free from bismine) was prepared freshly from time to time by redistilling an "AnalaR" sample. Other stock solutions of nitric acid, sodium nitrate, and potassium bromide and nitrate were made up from "AnalaR" reagents.

**General Procedure.**—The distribution ratio of indium [as defined by equation (1)] between *iso*butyl methyl ketone and a series of acid-bromide solutions was measured radiometrically by using  $^{114}\text{In}$  as tracer. Aqueous phases were made up from appropriate dilutions of stock solutions of radioactive indium in hydrobromic acid, hydrobromic acid, or alkali bromide and nitric acid, being added together with alkali-metal nitrate or perchlorate to maintain a constant salt background. Series of experiments were performed in which the total concentrations of indium, hydrogen, or bromide ions were varied in turn, the other two concentration variables being held constant. All measurements refer to systems at equilibrium, the rate of attainment of equilibrium being measured by observing the increase of the apparent distribution ratio with time of shaking. Under the experimental conditions employed a shaking time of 2–3 min. was always sufficient for the attainment of equilibrium, and a standard time of 5 min. was adopted.

Neither phase was pre-saturated with the other before equilibrium in the distribution experiments. 20 ml. of radioactive indium solution of known concentration in an acid-bromide

mixture of known composition and 20 ml. of *isobutyl methyl ketone* were pipetted into a 60-ml. Pyrex test-tube fitted with a ground-glass stopper. Equilibration was effected at room temperature ( $13^\circ \pm 3^\circ$ ) by mechanical shaking in a horizontal position for 5 min. at 150 cycles per min. B24 stoppers and test-tubes were carefully matched so that no losses occurred during the shaking. After equilibration, the tubes were placed upright, and the phases separated rapidly. Any globules of water entrapped at the air-ketone interface, or between the ketone and the walls of the tube, were dislodged by a sharp flick of the tube. The levels of the menisci were then noted on paper strips affixed to the outside of the tubes. After these had been emptied, washed, and dried, water was run in from a burette up to the marks to obtain the volumes of the organic and aqueous phases,  $V_0$  and  $V$ , after equilibration. The standard deviation of such measurements was found to be of the order of  $\pm 1\%$ . In the majority of the present experiments, the changes in phase volume on equilibration were not detectable within these limits.

The initial aqueous phase and the aqueous phase after equilibration were assayed radio-metrically by means of 20th Century Electronics Ltd. G.M.6 liquid counters. As mass balances of  $99.5 \pm 4.8\%$  were obtained in similar experiments in which aliquot parts of the organic phase were also analysed (Irving and Rossotti, *Analyst*, 1952, 77, 801), the assumption of a 100% mass balance in the present work was considered to be justified.

Under comparable conditions of counting we have

$$C' : C : C_o = R' : R : R_o. \quad \dots \quad (2)$$

where  $C$  denotes the concentration of indium and  $R$  the counting rate, superscript dashes refer to aliquot parts of initial solutions (before equilibration), and the subscript  $o$  denotes the organic phase. For 100% mass balance

$$V'C' = VC + V_oC_o \quad \dots \quad (3)$$

and combining equations (1), (2), and (3), we have

$$q = (V'R' - VR) / V_oR \quad \dots \quad (4)$$

The counting rates,  $R'$  and  $R$ , in this equation are corrected for the paralysis-time of the counting assembly, and for the background count (about 11 counts per min.). The duration of counting was always sufficient to give, at worst, a standard deviation of  $\pm 1\%$ . Since the miscibility of the organic phase and aqueous phase was negligibly small and constant over the range of acidities used in the present investigation, no corrections were needed for self-absorption provided aliquot parts were assayed in the same G.M.6 tube. Correction for the decay of the 49-day  $^{114}\text{In}$  was also unnecessary provided aliquots from any one experiment were assayed consecutively. For counting, 10 ml. of the equilibrium aqueous phase were transferred by pipette to the G.M.6 tube, great care being taken to avoid contamination by the (upper) ketonic phase. Aliquot portions of the aqueous phases, diluted where necessary, were also titrated with 0.1N-sodium hydroxide to determine the equilibrium acidity.

*Partition Experiments.*—All symbols used in the following Tables have been defined above. Within the limits of experimental error the initial and the final volumes of both aqueous and organic phases were 20.0 ml., unless there is a contrary statement.

1. *Rate of attainment of equilibrium.* For any one series of experiments this was investigated by shaking a number of tubes containing 20 ml. of *isobutyl methyl ketone* and 20 ml. of the same aqueous phase for varying lengths of time. Typical results are given in Table 1.

TABLE 1. *Rate of attainment of equilibrium of  $10^{-5}\text{M}$ -indium in 0.2N-hydrobromic acid.*

$t$ (min.)	0.5	2.0	3.0	5.0	10.0	30.0
$q$	0.935	1.043	1.067	1.076	1.067	1.071

2. *Dependence of distribution ratios upon the concentration of hydrogen ion, bromide ion, and hydrobromic acid.* Results are given in the following Tables.

3. *Analysis of organic extracts.* The organic extracts obtained by equilibration of solutions of low acidity were analysed in several cases for hydrogen, indium, and halide ions. A suitable aliquot portion of the organic phase was titrated with 0.1N-sodium hydroxide (thymol-blue as indicator), preliminary experiments having shown that the end-point was unaffected by the organic solvent. This gave the sum of hydrogen-ion concentration and three times the indium concentration. After acidification with dilute nitric acid, the bromide-ion concentration was determined by Volhard's method, control experiments having shown that the end-point was

TABLE 2. *Dependence of distribution on hydrogen-ion concentration.*

(a) [H <sup>+</sup> ]' .....	0.80	0.50	0.20	0.05	0.0016		
[H <sup>+</sup> ] .....	0.750	0.475	0.192	0.048	—		
q .....	0.35	0.245	0.191	0.125	0.105		
(b) [H <sup>+</sup> ]' .....	1.80	1.50	1.00	0.50	0.10	0.0116	0.0016
[H <sup>+</sup> ] .....	1.51	1.27	0.873	0.433	0.085	—	—
q .....	0.459	0.389	0.347	0.257	0.229	0.230	0.220

(a) Aqueous solutions for which [KBr] = 0.2M, and  $C_{In} = 7.92 \times 10^{-5}M$  with variable amounts of nitric acid, the ionic strength being brought up to 1.0M with potassium nitrate. (b) Solutions for which [NaBr] = 0.2M and  $C_{In} = 7.92 \times 10^{-5}M$  with variable amounts of nitric acid, the ionic strength being brought up to 2.0M with sodium nitrate.

TABLE 3. *Dependence of distribution ratio on bromide-ion concentration: potassium salts present.*

(a) [KBr] .....	1.0	0.7	0.5	0.4	0.2	0.1
q .....	1.31	0.650	0.426	0.330	0.105	0.0306
(b) [KBr] .....	0.80	0.50	0.40	0.35	0.25	0.20
q .....	8.22	2.81	1.22	0.620	0.313	0.191
[KBr] .....	0.10	0.05				
q .....	0.0307	0.0104				
(c) [KBr] .....	3.84	1.92	1.00	0.96	0.50	0.30
q .....	11.9	5.56	1.31	1.43	0.48	0.16
(d) [KBr] .....	4.00	2.50	2.40	1.20	0.68	0.50
q .....	18.7	30.0	39.6	20.5	6.55	3.21
[KBr] .....	0.40	0.25	0.20	0.15	0.10	
q .....	1.63	0.703	0.350	0.133	0.0662	

In the initial aqueous solutions  $C_{In} = 7.92 \times 10^{-5}M$  in each case. In runs (a) and (c) the concentration of hydrogen ions at equilibrium was 0.0016N, in (b) it was 0.20N, and in (d) it was 0.26N. In runs (c) and (d) the ionic strength was not controlled, but in series (a) and (b) it was kept at 1.0M by appropriate additions of potassium nitrate.

TABLE 4. *Dependence of distribution ratio on bromide-ion concentration: sodium salts present.*

(a) [NaBr] ...	1.00	0.75	0.50	0.25			
q .....	3.23	1.85	0.790	0.203			
(b) [NaBr] ...	0.80	0.50	0.25	0.10			
q .....	10.0	2.52	0.405	0.0264			
(c) [NaBr] ...	6.0	5.0	4.0	3.0	2.0	1.5	1.0
q .....	92.0	160	162	53.5	25.3	11.4	3.23
(d) [NaBr] ...	6.0	3.5	2.0	1.0	0.5	0.25	0.10
q .....	81.8	63.5	69.4	16.4	3.39	0.694	0.0853
(e) [NaBr] ...	1.00	0.70	0.50	0.35	0.20		
q .....	28.3	10.4	4.27	1.64	0.347		

In all these solutions  $C_{In} = 7.92 \times 10^{-5}M$ . In series (a) and (c) the concentration of hydrogen ions was 0.0016N, in series (b) and (d) it was 0.20N, and in series (e) 1.0N. The ionic strength was not controlled in series (c) and (d), but in series (a) and (b) it was maintained at 1.0M, and in series (e) at 2.0M by appropriate additions of sodium nitrate.

TABLE 5. *Dependence of the distribution ratio on the concentration of hydrobromic acid.*

	N'	N	V <sub>0</sub>	V	q		N'	N	V <sub>0</sub>	V	q
(a)	0.80	0.775	20.0	20.0	29.1	(b)	0.80	0.758	20.0	20.0	3.55
	0.60	0.57	20.0	20.0	7.61		0.60	0.550	20.0	20.0	1.15
	0.40	0.38	20.0	20.0	1.70		0.40	0.358	20.0	20.0	0.306
	0.20	0.20	20.0	20.0	0.210		0.20	0.175	20.0	20.0	0.0471
(c)	1.0	0.975	19.5	20.5	180						
	0.4	0.39	19.5	20.5	12.7						
	0.2	0.2	20.0	20.0	2.10						

In these experiments the concentration of indium was  $C_{In} = 5 \times 10^{-6}M$ . In series (c) no attempt was made to control the ionic strength. In series (a) and (b) it was kept at 1.0M by appropriate additions of potassium nitrate and sodium perchlorate, respectively.

unaffected by the presence of indium or organic solvent. Indium was determined as previously described. Although the indium : bromine ratios were 1 : 4 within the limits of experimental error (see Table 7), the concentration of hydrogen ions, calculated on the assumption that 1 mole of indium reacts with 3 g.-equiv. of hydroxide ion, was found to be zero. Since the analytical method was certainly capable of detecting equivalent concentrations of hydrogen ions in the presence of  $10^{-3}$  or  $10^{-2}$ M indium (cf. Irving and Rossotti, Part IV, *loc. cit.*), it is concluded that alkali-metal complexes of the  $\text{InBr}_4^-$  ion may undergo partition as well as the acido-species  $\text{HInBr}_4$ .

*Dependence of Distribution Ratio upon Metal Concentration.*—From the data presented in Table 6 it is clear that at each initial concentration of hydrobromic acid,  $N'$ , either in the presence or in the absence of potassium nitrate, the distribution ratio,  $q$ , is independent of the total metal concentration in the range up to  $C_{\text{In}} \sim 10^{-5}$ M. At higher metal concentrations the distribution ratios decrease (Part IV).

TABLE 6. *Distribution of indium bromide species between hydrobromic acid and isobutyl methyl ketone at low metal concentrations.*

Initial acidity, $N'$ .....	1.0	0.6	0.4			
Concn. of $\text{KNO}_3$ , M .....	0.0	0.4	0.6			
	$10^7 C_{\text{In}}$	$q$	$10^7 C_{\text{In}}$	$q$	$10^7 C_{\text{In}}$	$q$
	10.0	185	5.00	7.60	5.00	1.73
	50.0	180	50.0	7.61	50.0	1.70
	111.0	180	244.0	7.68	295.0	1.72

It follows from the general treatment of partition equilibria given previously (Part I) that the derivative  $(\partial \log q / \partial \log [\text{In}^{3+}]_{[\text{HBr}]})$  will only be zero when the (average) state of association is the same in both phases, and that under such conditions the derivative  $(\partial \log q / \partial \log C_{\text{In}})_{[\text{HBr}]}$  will also be zero. Since experiments (cf. Table 6) establish the latter for indium concentrations less than about  $10^{-5}$ M, it is reasonable to assume that at these low concentrations of metal all the species present are mononuclear. If this is the case, partition equilibria are independent of the concentration of free indium ions and hence, as found, of total metal concentration. In the following paper the presence of dinuclear indium complexes in the aqueous phases solutions is discussed: to avoid such complications indium concentrations of the order of  $10^{-5}$ M were used throughout the present work. It will be assumed that the species  $\text{In}^{3+}$ ,  $\text{InBr}^{2+}$ ,  $\text{InBr}_2^+$ ,  $\text{InBr}_3$ , and  $\text{InBr}_4^-$  exist in the aqueous phase together with the acido-complex  $\text{HInBr}_4$ . That no higher complexes exist in aqueous solution of hydrobromic acid of the strength employed here is supported by measurements of the stability constants (Carleson and Irving, *J.*, 1954, 4390, and refs. therein) and by comparison with the thoroughly investigated analogous system of  $\text{Fe}^{3+}$  and  $\text{Cl}^-$  (Gamlen and Jordan, *J.*, 1953, 1435).

*Variation of Distribution Ratio with Hydrogen-ion Concentration.*—Fig. 1 shows the results of measurements of distribution ratios for a series of solutions of constant total indium concentration in the presence of a constant excess of bromide ions, the concentration of hydrogen ions being varied. Nitric acid was used throughout as a source of hydrogen ions, preliminary experiments having shown that indium nitrate was not extracted into isobutyl methyl ketone. In series (a), 0.2M-potassium bromide was the source of bromide ions and the ionic strength was maintained at 1.0M by additions of potassium nitrate. In series (b), 0.2M-sodium bromide was used to provide bromide ions and the ionic strength was held at 2.0M by additions of sodium nitrate. In both cases  $(\partial \log q / \partial \log [\text{H}^+]_{[\text{Br}^-]})$  tends to zero at relatively high values of pH, and towards unity at low values.

In such experiments it is pertinent to consider the possible hydrolysis of the indium ion, for competitive complex formation between bromide and hydroxyl ions might be expected to decrease extraction continuously towards zero at or before the point at which indium hydroxide is precipitated. If we accept Moeller's data (*J. Amer. Chem. Soc.*, 1941, 63, 2625), precipitation of  $10^{-5}$ M-indium halide solutions would occur at  $\text{pH} \sim 5$ . The present experiments were conducted at acidities greater than  $\text{pH} = 3$  to give a margin of safety. The relative proportions of the species  $\text{InBr}^{2+}$  and  $\text{InOH}^{2+}$  at this pH in the presence of 0.2M-bromide ions can be estimated from the relevant stability constants.

Taking  $[\text{InBr}^{++}]/[\text{In}^{3+}][\text{Br}^-] = 103$  and  $[\text{InOH}^{++}]/[\text{In}^{3+}][\text{OH}^-] \sim 10^{10}$  (Carleson and Irving, *loc. cit.*, and refs. therein), we have  $[\text{InBr}^{++}]/[\text{InOH}^{++}] \sim 200$ , so that hydrolysis can be of only slight importance even at the highest pH used in this work.

If the species extracted into the organic phase contains no hydrogen (e.g.,  $\text{InBr}_3$ ,  $\text{NaInBr}_4$ , or  $\text{KInBr}_4$ ) the value of the derivative  $(\partial \log q / \partial \log [\text{H}^+])_{[\text{Br}^-]}$  will be zero at comparatively low concentrations of bromide ion, but will approach unity if  $\text{HInBr}_4$  has a high partition coefficient and is the predominant species in the organic phase. The present results confirm the predominance of  $\text{HInBr}_4$  as the species extracted at relatively high acidities. They also demonstrate that at lower acidities one or more other species can undergo partition in a manner which is independent of hydrogen-ion concentration. These may be  $\text{InBr}_3$ , or an alkali-metal complex,  $\text{AlInBr}_4$ , or a mixture of both. Although the differences in extraction from 1.0M-potassium salts or 2.0M-sodium salts containing 0.2M-bromide ion and a low hydrogen-ion concentration could be due to some activity effect,

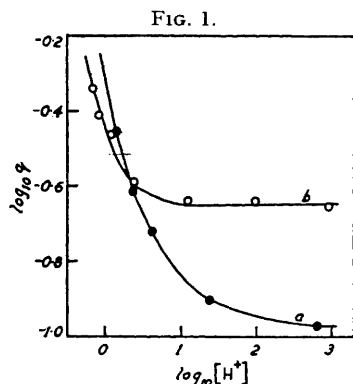


FIG. 1. Dependence of distribution ratio upon hydrogen-ion concentration. For curve *a*, initial aqueous phases contained 0.2M-potassium bromide, and the ionic strength was made up to 1.0M with potassium nitrate. For curve *b*, they contained 0.2M-sodium bromide, and the ionic strength was made up to 2.0M with sodium nitrate.

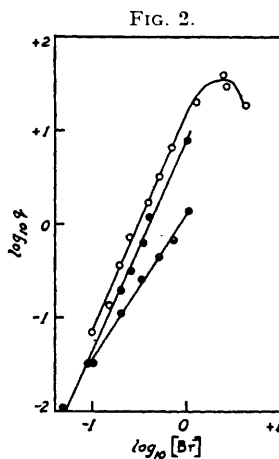


FIG. 2. Dependence of distribution ratio upon bromide-ion concentration. The hydrogen-ion concns. were 0.26N, 0.20N, and  $1.6 \times 10^{-2}$ N for open, full, and half circles, respectively. Potassium bromide was used as the source of bromide ions throughout, and the ionic strength was made up to 1.0M with potassium nitrate for the last two runs only.

the hypothesis that alkali-metal complexes can undergo partition is supported by recent work on the extraction of alkali-metal reineckates and per-rhenates into nitromethane (Friedman and Haugen, *J. Amer. Chem. Soc.*, 1954, **76**, 2060).

*Variation of Distribution Ratio with Concentration of Bromide Ions.*—Fig. 2 shows the results of measurements of distribution ratios for a series of solutions in which the concentration of indium and of hydrogen ions was the same, the concentration of bromide ion being varied. Nitric acid and potassium bromide were used as the source of these ions, and potassium nitrate was used to maintain an ionic strength of 1.0M in some experiments. Although the effect of the neutral salt is to decrease the extraction, the slopes of the plots of  $\log q$  against  $\log [\text{Br}^-]$  at constant hydrogen-ion concentration do not appear to be markedly affected by changes in the ionic strength of the medium. The values of the derivative  $(\partial \log q / \partial \log [\text{Br}^-])_{[\text{H}^+]}$  are 1.6, 2.3, and 2.4 for  $[\text{H}^+] = 0.0016$ , 0.20, and 0.26 g.-ion/l. respectively. From the equations deduced previously (Part I, *loc. cit.*) it is clear that the value of this derivative would be  $(3 - \bar{n})$  if  $\text{InBr}_3$  were the extractable species, and  $(4 - \bar{n})$  if the species  $\text{HInBr}_4$  or  $\text{AlInBr}_4$  passes on partition. If, then,  $\bar{n}$  is of the order of 1.6 for the whole range of bromide-ion concentrations explored, the experimental data favour the former hypothesis when  $[\text{H}^+] \sim 10^{-3}\text{M}$ , but the latter when  $[\text{H}^+] \geq 0.1\text{M}$ .

In a further series of experiments in which sodium bromide and nitrate replaced the corresponding potassium salts as the source of bromide ion and salt background respectively, comparable values of  $q$  were not greatly changed; but the values of the derivative  $(\partial \log q / \partial \log [\text{Br}^-])_{[\text{H}^+]}$  were identical (2.3) both at  $[\text{H}^+] = 0.2\text{M}$  and at  $0.0016\text{M}$ . This is explicable if the species being extracted at low acidities (and  $\bar{n} = 1.6$ ) is either  $\text{HInBr}_4$  or  $\text{NaInBr}_4$ . Only the latter hypothesis is consistent with observations on the dependence of  $q$  upon hydrogen-ion concentration discussed above. The feasibility of extracting indium-bromide species which do not contain hydrogen ions was further demonstrated by the successful extraction of indium from more concentrated bromide solutions at relatively high pH. Results collected in Table 7 show that the substantial amounts of indium ex-

TABLE 7. *Distribution of indium bromide species into isobutyl methyl ketone at low acidities.*

$C_{\text{KBr}}$	pH	$10^4 C_{\text{In}}$	$q$	$-\log C_0$	Analytical results for In : Br ratios
4.0	2.8	80.79	6.72	2.15	1 : 4.11 and 1 : 4.02
3.76	2.8	40.79	5.39	2.46	1 : 4.20 and 1 : 3.88
1.0	~4.2	2.528	0.876	3.60	
1.0	~4.2	25.03	0.497	2.60	
1.0	~4.2	250	0.250	1.60	

tracted were greater than the amount of hydrogen ion present to repress hydrolysis. Although analyses of the organic phases showed that the indium : bromine ratio was 1 : 4 within the limits of experimental error, no hydrogen was detectable. This result suggests that  $\text{KInBr}_4$  was the predominant species extracted under these particular experimental conditions.

*Variation of Distribution Ratio with Concentration of Hydrobromic Acid.*—Fig. 3 shows how the distribution ratio for indium at a fixed total concentration of  $5 \times 10^{-6}\text{M}$  varies with the concentration of hydrobromic acid. In one series of experiments (curve *c*) no inert salt was added. In another (curve *a*) an ionic strength of  $1.0\text{M}$  was maintained with potassium nitrate, with the result that distribution ratios were lower and the value of  $(\partial \log q / \partial \log C_{\text{HBr}})$  was increased.

The possibility that nitrate ions were forming complexes competitively with indium in the aqueous phase and so reducing extraction was tested by replacing (potassium) nitrate by (sodium) perchlorate which might be expected to complex least strongly of all anions. Experimental results (Fig. 3, curve *b*) showed that partition into the organic phase is actually reduced still further by this substitution, although the value of the slope  $(\partial \log q / \partial \log C_{\text{HBr}})$  is unaltered. This result disposes of the hypothesis of competitive complexing by nitrate ions but emphasises that additions of different "inert" salts will modify both (stoichiometric) partition coefficients and stability constants and not necessarily to an equivalent extent. The marked increase in the value of  $(\partial \log q / \partial \log C_{\text{HBr}})$  as the salt background is eliminated indicates the sensitivity of the results to the precise nature of the aqueous phase. There are innumerable examples of specific salt effects reported in the solvent extraction of inorganic materials (cf. Bock and Bock, *Z. anorg. Chem.*, 1950, **263**, 146; Jenkins and McKay, *Trans. Faraday Soc.*, 1954, **50**, 107). However, the possibility of the co-extraction of  $\text{KInBr}_4$  and  $\text{NaInBr}_4$  with partition coefficients lower than that of the acido-complex  $\text{HInBr}_4$  is another relevant factor.

In the absence of alkali-metal cations the value of the derivative  $(\partial \log q / \partial \log C_{\text{HBr}})$  is found to be 2.74 for free bromide-ion concentrations up to  $1.0\text{M}$ . With salt backgrounds of  $1.0\text{M}$  the value of this derivative is somewhat greater and equals 3.3 for hydrobromic acid concentrations below  $0.5\text{M}$  in the presence of either potassium nitrate or sodium perchlorate. Under identical experimental conditions  $(\partial \log q / \partial \log [\text{Br}^-])_{[\text{H}^+]}$  = 2.3. From the general treatment given in Part I the theoretical value of these derivatives would be  $(5 - \bar{n})$  and  $(4 - \bar{n})$ , respectively, were  $\text{HInBr}_4$  the predominant extractable species at relatively high acidities. This hypothesis is therefore confirmed, provided it can be shown that the degree of formation of the system is of the order  $\bar{n} = 1.7-2.3$  for free bromide-ion concentrations in the range  $0.1-0.5\text{M}$ .

*Correlation of Partition and Stability Data.*—The complexes which indium forms with bromide ions are comparatively weak, and by using an ion-exchange technique it has proved possible only to obtain the following over-all stability constants,  $\beta_1 = 103$ ,

TABLE 8. *Percentage degrees of formation of indium bromide complexes, assuming  $\beta_1 = 103$ ,  $\beta_2 = 1250$ ,  $\beta_3 = 1900$ , and  $\beta_4 = 200$ .*

$-\log [\text{Br}^-]$	$\bar{n}$	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$
2.0	0.60	46.38	47.78	5.75	0.88	$9.28 \times 10^{-5}$
1.0	1.60	3.90	40.20	48.40	7.42	0.0781
0.7	1.92	1.15	23.75	57.20	17.53	0.3690
0.5	2.13	0.46	14.83	56.45	27.35	0.9107
0.25	2.39	0.12	7.16	48.48	41.77	2.472
0.1	2.54	0.05	4.31	41.24	50.20	4.197
0.0	2.64	0.03	2.99	36.00	55.17	5.807

TABLE 9. *Corresponding values of  $q$  and  $p_4 K^{\text{H}}$  for the distribution of  $\text{HInBr}_4$  between isobutyl methyl ketone and hydrobromic acid.*

$q$ .....	158.5	84.1	33.5	6.92	2.11
$10^{-3} p_4 K^{\text{H}}$ .....	2.73	2.53	2.41	2.40	2.86

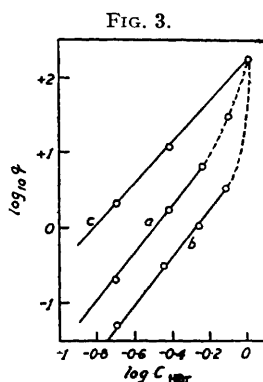


FIG. 3. *Dependence of distribution ratio upon hydrobromic acid concentration.* The ionic strength was made up to 1.0M with potassium nitrate and with sodium perchlorate for curves *a* and *b*, respectively. No salt background was used for curve *c*.

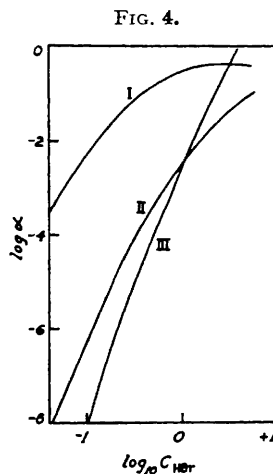


FIG. 4. *The degree of formation of some indium bromide complexes.* I,  $\text{InBr}_3$ ; II,  $\text{InBr}_4^-$ ; III,  $\text{HInBr}_4/K^{\text{H}}$ . The ordinate of the curve for  $\text{HInBr}_4$  is displaced by  $\log K^{\text{H}}$ .

$\beta_2 = 1250$ , and  $\beta_3 = 1900$ , which are valid for a medium of ionic strength 0.7M (perchloric acid) at 20° (Carleson and Irving, *loc. cit.*). These correspond to step-formation constants of  $K_1 = 103$ ,  $K_2 = 12.1$ , and  $K_3 = 1.5$ . Since the ratio  $K_n/K_{n-1}$  is approximately 8, we may assume that  $K_4 < 0.2$ , a value which may be greatly overestimated if the trend of values resembles that for the ferric chloride complexes (Gamlen and Jordan, *loc. cit.*). The degree of formation of individual complexes,  $\alpha_n = [\text{InBr}_n^{3-n}]/C_{\text{In}}$ , and the average ligand number,  $\bar{n}$ , have been calculated for various concentrations of free bromide ion on the assumption that  $\beta_4 = 200$ . Table 8 shows that, even at the highest concentration of free bromide ion (1M) used in the extractions, the species  $\text{InBr}_4^-$  is a minor constituent of the aqueous phase. Unless, therefore, the acido-complex is a very weak acid, which appears unlikely (cf. ferrocyanic acid; Nekrassov and Zotov, *J. Appl. Chem. U.S.S.R.*, 1941, 14, 264; cf. *Chem. Abs.*, 1941, 35, 1834), its partition coefficient,  $p_4$ , must be very large. The magnitude of the product  $p_4 K^{\text{H}}$  (where  $K^{\text{H}} = [\text{HInBr}_4]/[\text{H}^+][\text{InBr}_4^-]$ ) can be computed from the experimental data for media from which alkali cations are absent if it is postulated



that only the uncharged species  $\text{HInBr}_4$  and possibly  $\text{InBr}_3$  are extracted. It then follows that

$$q = p_3\alpha_3 + p_4\alpha_4K^{\text{H}}[\text{H}^+] \dots \dots \dots (5)$$

Using values of  $q$ , and corresponding values of  $\alpha_3$  and  $\alpha_4$  from Table 8, we can set up simultaneous equations and solve for  $p_3$  and  $p_4K^{\text{H}}$ . It is at once evident that  $p_3$  is negligibly small, *i.e.*, that the extraction of indium tribromide can be neglected in comparison with that of acido-species,  $\text{HInBr}_4$ , under conditions of high acidity. Table 9 gives the results of these computations which lead to a mean value of  $p_4K^{\text{H}} = 2600 \pm 180$ . Naturally any estimate of this product will depend upon the value of  $\alpha_4$  used in its calculation, and this in turn depends upon values taken for the stability constants. The possible effect of underestimating the value of  $K_2$  and overestimating the value of  $K_4$  is shown in Table 10. Although the changes make very little difference to values of  $\bar{n}$  at corresponding concen-

TABLE 10. *Percentage degrees of formation of indium bromide complexes, assuming  $\beta_1 = 114$ ,  $\beta_2 = 2270$ ,  $\beta_3 = 4450$ , and  $\beta_4 = 89$ .*

$-\log [\text{Br}^-]$	$\bar{n}$	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$
2.0	0.68	42.18	48.08	9.57	0.19	$5.54 \times 10^{-5}$
1.0	1.77	2.53	28.82	57.38	11.25	0.025
0.7	2.07	0.67	15.16	60.39	23.67	0.093
0.5	2.26	0.25	8.89	55.96	34.69	0.22
0.25	2.47	0.06	4.05	45.34	49.98	0.56
0.1	2.58	0.03	2.39	37.80	58.85	0.93
0.0	2.65	0.01	1.65	32.78	64.27	1.28

*Corresponding values of  $q$  and  $p_4K^{\text{H}}$  calculated with these alternative stability constants.*

$q$ .....	84.1	33.5	6.92	2.11	0.299
$10^{-4}p_4K$ .....	1.14	1.085	1.00	1.035	1.095

trations of free bromide ions, yet values of  $\alpha_4$  are reduced from two- to four-fold, and computed values of  $p_4K^{\text{H}}$  now have a mean value of  $10,700 \pm 500$ . That there is no serious drift in values of  $p_4K^{\text{H}}$  calculated in Tables 9 and 10 suggests that the general treatment cannot be seriously at fault and places the value of this product as of the order  $10^3$ — $10^4$ . A similar treatment of published data for the extraction of ferric chloride from hydrochloric acid shows that the extraction of the species  $\text{HFeCl}_4, \text{aq.}$  is substantial although the ion  $\text{FeCl}_4^-$  forms only a minor constituent of the aqueous phase at moderate acidities.

The variation of  $\alpha_3$  (the fraction of the total indium present as  $\text{InBr}_3$  in the aqueous phase) and of  $\alpha_4$  (the fraction present as  $\text{InBr}_4^-$ ) with changes in the concentration of bromide ion is shown as a double logarithmic plot in Fig. 4. These data are calculated by using the stability constants quoted in Table 8. The product  $\alpha_4[\text{H}^+]$  is proportional to the concentration of acido-complex and its variation with the total concentration of hydrobromic acid is also shown as a double logarithmic plot in Fig. 4.

It will be noted that the curvature of all the plots is slight over the range of concentrations, *viz.*,  $0.1 < [\text{Br}^-] < 1.0\text{M}$ , used in the present extraction studies. From the data calculated in Tables 8 and 10, values of  $\bar{n}$  are seen to be comparatively insensitive to moderate changes in values adopted for stability constants over the same range of bromide-ion concentrations. Use of the preferred set of data (Table 8) shows  $\bar{n}$  to increase from 1.6 to 2.64 as  $[\text{Br}^-]$  increases from 0.1 to 1.0M. The mean value of 2.12 agrees well with the value,  $\bar{n} = 2.26$ , deduced from the experimental value  $(\partial \log q / \partial \log [\text{HBr}]) = 5 - \bar{n} = 2.74$  found in this range for a medium containing no alkali-metal cations. The agreement again justifies the application of the idealised equations deduced in our general treatment (Part I, *loc. cit.*) to the solvent extraction of indium bromide.

For media which contain alkali-metal cations the experimentally determined values for  $(\partial \log q / \partial \log [\text{Br}^-])$  when  $[\text{H}^+] = 0.0016\text{M}$ , for  $(\partial \log q / \partial \log [\text{Br}^-])$  when  $[\text{H}^+] = 0.2\text{M}$ , and for  $(\partial \log q / \partial \log [\text{HBr}])$ , are 1.6, 2.3, and 3.3, respectively. These may be compared with the values of 1.4, 2.4, and 3.4 for  $(\partial \log \alpha_3 / \partial \log [\text{Br}^-])$ ,  $(\partial \log \alpha_4 / \partial \log [\text{Br}^-])$ , and  $(\partial \log \alpha_4[\text{H}^+] / \partial \log [\text{HBr}])$  found at a free ligand concentration of  $[\text{Br}^-] = 0.1\text{M}$ , which also corresponds to the degree of formation of the system of  $\bar{n} = 1.6$ . This correspondence with

the average ligand number obtaining at the lowest free-ligand concentrations used in the actual extractions suggests that some additional factor is operating to make extraction increase at a greater rate with bromide concentration than predicted theoretically. The marked increase in the value of the derivative ( $\partial \log q / \partial \log C_{\text{HBr}}$ ) as the salt background is eliminated (Fig. 3) suggests that some specific-ion effect may be operative, and that activity coefficients were not adequately held constant in the aqueous phase, the nature of which changes substantially over the range of extraction conditions. Alternatively, the estimated value of  $\beta_4$  may be seriously at fault: it must also be emphasised that the experimental values of  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  correspond to a different ionic strength (0.7M-perchloric acid) and a slightly different temperature (20°). It is, however, worth considering whether it is possible to interpret the values of distribution ratios in the presence of varying salt backgrounds on the assumption that the alkali-metal complexes  $\text{AlnBr}_4$  ( $A = \text{Na}$  or  $\text{K}$ ) are co-extracted.

Equation (5) may be extended as follows:

$$q = p_3 \alpha_3 + p_4 \alpha_4 K^{\text{H}} [\text{H}^+] + p_A \alpha_4 K^{\text{A}} [\text{A}^+] \quad . \quad . \quad . \quad (6)$$

where  $p_A$  is the partition coefficient and  $K^{\text{A}}$  the stability constant of the species  $\text{AlnBr}_4$ . In Table 11 results of calculations are shown on the assumption (i) that only  $\text{InBr}_3$  and  $\text{HInBr}_4$  are co-extracted, and (ii) that only  $\text{HInBr}_4$  and  $\text{AlnBr}_4$  are co-extracted. As expected, there are substantial drifts in the calculated values of the parameters though these are greater for a background of sodium nitrate than one of potassium nitrate, and

TABLE 11. Calculations from data for the extraction of indium from hydrobromic acid solutions containing alkali cations.

-log [Br <sup>-</sup> ]	Potassium nitrate				Sodium nitrate			
	$p_3$	$p_4 K^{\text{H}}$	$p_4 K^{\text{H}}$	$p_{\text{K}} K^{\text{K}}$	$p_3$	$p_4 K^{\text{H}}$	$p_4 K^{\text{H}}$	$p_{\text{Na}} K^{\text{Na}}$
0.7	0.572	123	150	26.7	0.656	115	145	30.8
0.5	0.765	174	197	22.7	1.06	189	220	31.1
0.25	1.22	319	330	20.1	2.53	345	388	41.5
0.1	1.99	464	485	20.4	4.56	515	570	52.0
0.0	2.44	600	600	21.6	7.1	700	700	65.4
Assumption	(i)		(ii)		(i)		(ii)	

greater on assumption (i) than on assumption (ii). It appears that the extraction of the alkali-metal complex  $\text{AlnBr}_4$  relative to that of the tribromide is greater in systems containing sodium than in those containing potassium ions, a conclusion in keeping with deductions made above from values of ( $\partial \log q / \partial \log [\text{Br}^-]$ ). Similar calculations with the alternative sets of stability constants used in Table 10 gave values of the various parameters which showed very much larger drifts, though the order  $p_4 K^{\text{H}} > p_{\text{Na}} K^{\text{Na}} > p_{\text{K}} K^{\text{K}} \gg P_3$  remained unchanged. Our calculations of  $\alpha_3$  and  $\alpha_4$  have assumed that the degrees of formation of the complexes  $\text{InBr}_3$  and  $\text{InBr}_4^-$  are unaffected by the presence of hydrogen ions or alkali-metal ions, *i.e.*, that  $K^{\text{H}}$  and  $K^{\text{K}}$  are small. The departures from the behaviour predicted theoretically may be due to extensive association of proton or alkali metal with the ion  $\text{InBr}_4^-$  in the aqueous phase, or to failure to hold activity coefficients constant, or to real variations in the values of the (stoichiometric) partition coefficients and stability constants under the range of experimental conditions.

*Discussion.*—The present experiments emphasise some of the fundamental difficulties encountered in examining the solvent extraction of inorganic salts. When studying the extraction of a metal as a stable inner complex,  $\text{ML}_n$ , of a weak monobasic acid, HL, the extractability can be investigated over a wide range of pH or HL. Activity coefficients can be held reasonably constant if there is a sufficient salt background in the aqueous phase, for only an uncharged species passes on partition into the organic phase. Other simplifying features of such systems are the extraction of a single species of such high stability that, at low free-ligand concentrations, a study of the derivatives ( $\partial \log q / \partial \log [\text{H}^+]_{[\text{M}]}$ ) or ( $\partial \log q / \partial \log [\text{L}]_{[\text{H}^+]}$ ) gives immediately and unequivocally the nature of the dissolved species. Furthermore, there is no evidence as yet of complications due to polynuclear species (cf. Part IV).

In comparable studies of the solvent extraction of inorganic salts the effect of acids in increasing phase miscibility sets an upper limit to the concentration of ligand which can be reached experimentally (Parts I, II, and V). But much lower concentrations may be desirable if phase compositions are not to be drastically modified. The species extracted may be a minor constituent of the mixture of complexes present in the aqueous phase—as we have demonstrated in the present instance—and present in amounts sufficient to give a readily measurable distribution ratio only at high ligand concentrations. Attempts to hold activity coefficients constant in the aqueous phase by providing a still higher concentration of a neutral salt (*e.g.*, an alkali-metal nitrate or perchlorate) may not be entirely effective in concentrations where the Debye-Hückel theory does not apply and where specific salt effects may dominate the situation. Furthermore, owing to their high tendency to solvation, alkali-metal salts may further reduce the activity of water in the aqueous phase, so hindering the extraction of hydrated species. Partition coefficients and stability constants will change in consequence of changes in the characteristics of the phase. The cations of the added “neutral” salt may compete with protons and form ion-pairs which also undergo partition. Its anions may form complexes in competition with the metal being studied and change its extractability.

In order to make any reliable deductions from variations in extractability with, *e.g.*, pH and free-ligand concentration, they must be varied over sufficiently wide limits, other factors being held constant. Although we have indicated above why attempts to do this may introduce unexpected complications, yet a consistent picture of the extraction of indium into *isobutyl methyl ketone* results from the assumption that more than one species is co-extractable. Provided  $[H^+] > 0.1M$ , the predominant species is  $HInBr_4, aq.$ , but at lower acidities the extraction of both indium tribromide and the alkali-metal complexes  $NaInBr_4$  and  $KInBr_4$  may become significant. Although the Raman spectrum of  $InBr_4^-$  has been found in organic extracts from both acid and essentially neutral solutions of indium and bromide ions (Woodward and Bill, to be published), the possible presence of some indium tribromide could be not disclosed by this technique.

It has generally been assumed that only an acido-complex is extracted from solutions of trivalent metals in halogen acids, although observations which show that other species may play an important rôle are to be found in the literature. Thus a close analogy to the present system is found in the extraction of thiocyanates of many metals where the partition of both the normal salt  $M(CNS)_3$  and the complex salts  $(NH_4)_3M(CNS)_6$  into diethyl ether ( $M = Fe^{3+}, Al^{3+}, Ga^{3+},$  and  $In^{3+}$ ) has been demonstrated under different experimental conditions (Bock, *loc. cit.*). Gold has been extracted from bromide solutions into *isobutyl methyl ketone* and into ethyl acetate (McBryde and Yoe, *Analyt. Chem.*, 1948, 20, 1094), and gallium from chloride solutions into ethyl methyl ketone (Milner, Wood, and Woodhead, *Analyst*, 1954, 79, 272) in the absence of halogen acid. Nekrassov and Ovsyankina (*J. Gen. Chem. U.S.S.R.*, 1941, 11, 573; *Chem. Abs.*, 1941, 35, 7266) have shown that ferric chloride is extracted from solutions containing no great excess of hydrogen ions. Equilibrium in these systems was interpreted in terms of the simultaneous extraction of the species  $H[FeCl_4(H_2O)_2]$  and  $H[FeCl_3(OH)(H_2O)_2]$ , but there appears to be no convincing evidence for not formulating the latter simply as  $FeCl_3, aq.$  In such systems where two or more species may be coextracted it is quite clear that the relative proportions passing into the organic phase will depend upon their relative partition coefficients and will be very sensitive to the relevant concentration variables of the aqueous phase as shown by equation (6). Conditions under which one or other species predominates in the organic extract may be accessible to experimental study, but the range where their contributions to the total extraction approach equality is likely to be too restricted for investigation.

We thank the Royal Society for the loan of apparatus, Imperial Chemical Industries Limited for a grant for the purchase of radio-nuclides, and the Department of Scientific and Industrial Research for a maintenance grant to one of us (F. J. C. R.).