*The Extraction of the Indium Halides into Organic Solvents.**

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The extraction of indium at tracer concentrations from solutions in hydrochloric, hydrobromic, and hydriodic acid into ten organic solvents has been studied as a function of the concentration of halogen acid. Extraction into fifteen other solvents has been examined in less detail. The predominant species extracted is the hydrated acido-complex, $HInX_4$,aq. ($X = Cl$, Br, or I). In any one solvent the halides are extracted in the order iodide > bromide > chloride. For all three solutes, the effectiveness of those solvents studied in detail falls in the order methyl propyl (or *iso*propyl) ketone > *iso*butyl methyl ketone > furfuraldehyde > ethyl acetate > diethyl ether > *iso*pentyl alcohol > *iso*pentyl acetate > 2 : 2′-dichlorodiethyl ether > di*iso*propyl ether. These phenomena, and the partition equilibria are discussed in terms of the general treatment of the solvent extraction of inorganic solutes proposed in Part I.

In a recent study of the solvent extraction of the halides of group IIIB metals (Irving and Rossotti, *Analyst*, 1952, **77**, 801) it was shown that, while indium may be almost quantitatively extracted by diethyl ether from hydrobromic acid or hydriodic acid, not more than 2·5% is extractable from hydrochloric acid if the phase volumes are initially the same. This work has now been extended to a detailed study of the extraction of indium from the three halogen acids with the object of ascertaining the relative efficiencies of extraction of different solvents for each halide in turn, of measuring the extent to which the relative extractabilities of the three indium halides vary from solvent to solvent, and of

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* Part V of a group of papers of which Parts I—IV are the preceding papers.

correlating the new results with previous observations on the solvent extraction of other types of inorganic salts.

Several workers have reported on the extraction of indium halides by diethyl ether (Ato, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1934, **24**, 162; Wada and Ishii, *ibid.*, p. 135; Kitahara, *Reports Sci. Res. Inst.* (*Japan*), 1948, **24**, p. 454; Bock, Kusche, and Bock, *Z. analyt. Chem.*, 1953, **138**, 167; Irving and Rossotti, *loc. cit.*). The extraction of indium from hydrobromic acid into *iso*propyl ether and from hydrochloric acid containing potassium iodide into ethyl acetate (Hudgens and Nelson, *Analyt. Chem.*, 1952, **24**, 1472), has been used analytically. Knox and Spinks (*Canad. Chem. Processing Ind.*, 1946, **30**, No. 11, 85) have reported on the extraction of concentrated solutions of indium in 6N-hydrochloric acid into a variety of organic solvents, and detailed studies have recently been made of the solvent extraction of indium from hydrobromic acid into *iso*butyl methyl ketone (Parts III and IV). The concentrations of indium employed in these investigations have ranged from 10^{-6}M to 6M; in some cases the extraction has not been studied over a range of acid concentrations, in others it is impossible to calculate values for distribution coefficients and for the acidities of the aqueous phases at equilibrium from the incomplete published data. Detailed comparison of results is thus frequently impossible.

In the present work the solvents studied in detail were chosen from commercially available ketones, aldehydes, esters, alcohols, and ethers. They were methyl propyl, methyl *iso*propyl, and *iso*butyl methyl ketone, furfuraldehyde, ethyl acetate, *iso*pentyl acetate, *iso*pentyl alcohol, and diethyl, di*iso*propyl, and 2 : 2′-dichlorodiethyl ether. A few experiments were made with *n*-butaldehyde, *cyclo*hexanone, nitromethane, nitrobenzene, and benzonitrile, all of which appeared to extract indium efficiently from its solutions in halogen acids. Hydrocarbons and chlorinated hydrocarbons were not investigated in such detail, but their ability to extract indium was consistently extremely low and generally negligible. Solvents of that type examined included benzene, toluene, xylene, *n*-hexane, *cyclo*hexane, chloroform, carbon tetrachloride, dichloroethane, and chlorobenzene. Carbon disulphide also appeared to be incapable of extracting indium.

For each system the initial and final acidities of the aqueous phase, N' and N, the initial and final volume of the aqueous phase, V' and V, and the initial and final volume of the organic phase, V_o' and V_o, were measured. The percentage of indium extracted, and the distribution ratio, q, were determined radiometrically with ^{114}In as tracer. In all the present experiments the volumes of the aqueous and the organic phases before equilibration were made equal ($V_o' = V'$), and neither phase was pre-saturated with the other. Here and elsewhere, the subscript, o, is used to distinguish quantities referring to the organic phase from those referring to the aqueous phase. The prime (*e.g.*, in V') is used to distinguish the values of phase volumes, acidities, counting rates, etc., before equilibration from the corresponding values after equilibration; this reverses the less satisfactory convention adopted in Part III.

The initial concentration of acid, N', was varied until it approached a value at which the phases became completely miscible. Owing to the large range of acidities thus investigated it was impossible to maintain the ionic strength of the aqueous phase at a constant value. Ideally, a complete study would include measurements of distribution ratios in which the concentration of indium is varied widely for each system; but here the concentrations of indium were maintained in the region of 10^{-5}M throughout. The effects of changes in metal concentration and in other variables have been investigated in detail for the system hydrobromic acid–*iso*butyl methyl ketone and are reported elsewhere (Parts III and IV). To assist in interpreting the results, the effect of changes in the concentration of halogen acids in the aqueous phase upon the solubility of water in certain of the organic phases was studied.

Values of the distribution ratio, q, and the percentage extraction, E, were calculated from the expressions:

$$q = C_o/C \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$E = 100V_oC_o/(V_oC_o + VC)$$
$$= 100qR/(1 + qR) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where C_o, C refer to the total concentration of indium in any form in the organic and the aqueous phase, respectively, after equilibration, and $R = V_o/V$ is the ratio of the phase volumes after equilibration. Care was taken that all measurements referred only to systems at equilibrium. The rate of attainment of equilibrium was followed by observing the rate of increase (or decrease) of radioactivity in the organic (or aqueous) phase respectively, or in the apparent change in distribution ratio with the time of shaking. Under the experimental conditions finally adopted (below), 2—3 min. proved sufficient for the attainment of equilibrium and a standard time of shaking of 5 min. was adopted throughout. Such a short period is in agreement with previous observations on the extraction of other inorganic salts (cf. Nachtrieb and Conway, *J. Amer. Chem. Soc.*, 1948, **70**, 3547; Wylie, *J.*, 1951, 1474) but is in striking contrast with the long periods of equilibration needed for the solvent extraction of metals as inner complexes with, *e.g.*, oxine, cupferron, and dithizone (Dyrssen, *Svensk Kem. Tidskr.*, 1953, **65**, 43; Irving, Bell, and Williams, *J.*, 1952, 356).

EXPERIMENTAL

Materials.—Radioactive ^{114}In (half-life 49 days) was obtained by irradiation of "Specpure" indium wire of known weight for periods up to two months at the Atomic Energy Research Establishment, Harwell, at a flux of 8×10^{11} neutrons cm.$^{-2}$ sec.$^{-1}$. A stock solution of concentration $3{\cdot}4 \times 10^{-2}$M in N-sulphuric acid was obtained by dissolving the irradiated metal in hot 6N-sulphuric acid. For extraction experiments the stock solution was diluted to give solutions of a convenient level of activity.

Ethers were tested for the absence of peroxides, and purified if necessary by standard methods (Weissberger and Proskauer, "Organic Solvents," Oxford, 1935). Catechol (50 mg./l.) was added to the *iso*propyl ether as a stabilising agent and the stocks were kept in the dark. Peroxidation of 2 : 2′-dichlorodiethyl ether was so rapid that purification and distillation was necessary immediately before use. Furfuraldehyde was redistilled and stabilised with catechol. The remaining solvents were of a good laboratory grade and were redistilled before use.

Hydriodic acid was redistilled over red phosphorus in an atmosphere of nitrogen within a day of use and stored in the dark. Good laboratory grades of hydrochloric acid, and of bromine-free hydrobromic acid were available.

General Procedure.—In the distribution experiments neither phase was presaturated with the other. Indium solutions of the desired concentration in halogen acid (20 ml.) and organic solvent (20 ml.) were introduced into a 60-ml. Pyrex glass test-tube fitted with a carefully ground-in B24 stopper. Equilibration was effected by mechanical shaking in a horizontal position for 5 min. at 150 cycles per minute. The tubes were then placed vertically and the phases allowed to separate completely at room temperature (13° ± 3°). This was rapid in most systems, but occasionally some minutes and even hours were necessary for complete separation (cf. p. 1963). The levels of the menisci were marked on vertical paper strips affixed to the outsides of the tubes. After the tubes had been emptied, washed, and thoroughly dried, water was run in from a burette up to the marks and the values of the phase volumes after equilibration, V_o and V, were so obtained. The standard deviation of such measurements was found to be 0·5—1·0%. Aliquot portions of each phase were removed in calibrated pipettes for analysis, great care being taken to avoid any contamination of one phase by the other.

Indium analyses were made by radio-assay of ^{114}In using 20th Century Electronics G.M.6 liquid counters. For the comparatively volatile solvents such as diethyl and di*iso*propyl ether and ethyl acetate, the oxine precipitation method described previously (Irving and Rossotti, *Analyst*, 1952, **77**, 801) was employed. With the other solvents aliquots of the initial and the equilibrated aqueous phases only were analysed and the activity in the organic phase was obtained by difference. Under comparable conditions of counting, $C' : C : C_o = Z' : Z : Z_o$, where Z is the counting rate corrected for paralysis time and background. As the radioactive indium was assayed in a standard solution no self-absorption corrections were necessary in the oxine procedure. Correction for decay of the comparatively long-lived ^{114}In was also unnecessary provided aliquot portions for any one experiment were assayed consecutively. The duration of counting was always sufficient to give a standard deviation of 1% or less. For mass balance, $V'C' = VC + V_oC_o$, thus permitting a check on experimental procedures (Irving and

Rossotti, *loc. cit.*). Equilibrium acidities were determined by dilution of aliquots and titration with 0·1N-sodium hydroxide.

Attainment of Equilibrium.—This was confirmed for any one solvent by shaking a number of identical samples of organic and aqueous phase for various times. Typical results are shown below. As equilibration was always attained in the order of 2—3 min., a shaking time of 5 min. was considered adequate and adopted throughout.

Extraction of indium by diethyl ether from 2N-*sulphuric acid containing* 0·1M-*potassium iodide.*

Time (min.)	0·5	1·0	1·5	2·0	5·0	10·0
Z (counts per min.)	8,142	11,267	11,500	12,484	12,484	12,494

Results of Partition Experiments.—In the following Tables N′, N are the normalities of the aqueous phase before and after equilibration, V and V_0 the volumes of the aqueous and organic phases after equilibration, and q and E the distribution ratio and the percentage of indium extracted into the organic phase as defined by equations (1) and (2). Before equilibration the aqueous and organic phases were of equal volume, $V_0' = V' = 20$ ml. Each solvent is designated by a Roman numeral to facilitate reference to later Tables.

Determination of the Water Content of the Organic Phase.—The dependence of the equilibrium concentration of water in the organic phase upon the concentration of halogen acid in the aqueous phase was determined for systems involving hydrochloric (and hydrobromic) acid and diethyl ether, di*iso*propyl ether, ethyl acetate, *iso*pentyl acetate, and *iso*pentyl alcohol. Aliquot parts of the organic phase, after equilibration, were analysed for water by the Karl Fischer method (*Angew. Chem.*, 1935, **48**, 394). The titration apparatus described by Bonner (*Analyst*, 1946, **71**, 483) was constructuted by Mr. A. Jenkins. Minor modifications included provision for magnetic stirring and a siphon for the removal of solutions, after titration, under pressure of dry nitrogen. The automatic burettes and reservoirs were fitted with guard tubes of magnesium perchlorate, and the nitrogen was dried by passage through a tower of silica gel. Platinum

II. *Methyl propyl ketone.*

(a) 5·14 × 10^{-5}M-*Indium in* HCl.

N′	N	V_0	V	E	q
0·20	0·186	18·5	21·5	0	0
0·375	0·36	18·9	21·1	7·2	0·0869
0·75	0·70	19·1	20·9	20·6	0·284
1·0	0·95	18·8	21·2	35·4	0·618
1·5	1·40	18·45	21·55	61·9	1·894
2·0	1·84	18·25	21·75	78·9	4·46
3·0	2·74	18·1	21·9	93·5	17·5
4·0	3·50	17·6	21·4	97·3	44·3
6·0	3·86	9·25	30·75	96·0	80·0

(b) 5·14 × 10^{-5}M-*Indium in* HBr.

N′	N	V_0	V	E	q
0·025	0·024	18·9	21·1	2·3	0·0263
0·05	0·048	18·85	21·15	12·3	0·158
0·10	0·095	18·9	21·1	45·0	0·915
0·20	0·190	18·9	21·1	83·2	5·53
0·40	0·379	18·9	21·1	97·0	36·2
1·00	0·92	18·2	21·8	99·8	516
3·50	2·52	14·3	25·7	99·9	1121
4·00		Completely miscible			

(c) 5·14 × 10^{-5}M-*Indium in* HI.

N′	N	V_0	V	E	q
0·0025	—	18·9	21·1	1·7	0·0188
0·0050	—	18·7	21·3	11·9	0·1535
0·010	—	18·7	21·3	60·1	1·716
0·015	—	18·65	21·3	86·0	7·02
0·020	—	18·9	21·1	93·6	16·3
0·025	—	18·9	21·1	97·75	48·6
0·050	—	18·7	21·3	99·7	377·5
2·0	1·375	19·4	20·6	99·7	386
2·5		Completely miscible			

III. *Methyl* iso*propyl ketone.*

(a) 5·14 × 10^{-5}M-*Indium in* HCl.

N′	N	V_0	V	E	q
0·10	0·092	18·3	21·7	0	0
0·25	0·24	18·45	21·55	1·8	0·0214
0·50	0·455	18·4	21·6	7·3	0·0925
0·75	0·71	18·7	21·3	23·0	0·340
1·00	0·91	18·5	21·5	38·1	0·716
1·50	1·38	18·3	21·7	64·1	2·12
2·00	1·81	17·9	21·15	79·6	4·84
3·00	2·70	17·7	22·3	93·9	19·5
4·00	3·38	16·4	23·7	97·3	51·9
6·00	3·78	8·3	31·8	97·1	127·7

(b) 5·14 × 10^{-5}M-*Indium in* HBr.

N′	N	V_0	V	E	q
0·02	—	18·4	21·6	0	0
0·03	—	18·4	21·6	3·6	0·044
0·05	—	18·2	21·8	12·2	0·166
0·10	0·093	18·5	21·5	49·5	1·14
0·20	0·186	18·6	21·5	86·0	7·07
0·375	0·350	18·4	21·6	96·8	35·6
1·00	0·90	17·9	22·1	99·8	535
3·00	2·41	15·0	25·0	99·9	1362
4·00	2·16	2·95	37·0	63·4	21·7

(c) 5·14 × 10^{-5}M-*Indium in* HI.

N′	N	V_0	V	E	q
0·0025	—	18·45	21·55	0	0
0·0050	—	18·3	21·7	6·8	0·0864
0·010	—	18·4	21·6	45·5	0·982
0·015	—	18·4	21·6	71·1	2·89
0·020	—	18·3	21·7	86·7	7·74
0·025	—	18·35	21·65	89·9	10·5
0·050	—	18·2	21·8	99·4	202·2
2·50	2·10	16·25	23·75	99·2	186·5

IV. iso*Butyl methyl ketone.*

(a) 5·14 × 10^{-5}M-*Indium in* HCl.

N′	N	V_o	V	E	q
0·105	0·10	20·0	20·0	1·1	0·0113
0·51	0·50	20·3	20·1	4·8	0·0495
1·00	0·976	19·65	20·4	6·8	0·0755
1·50	1·45	20·15	20·3	32·2	0·478
2·04	2·00	19·5	20·65	53·2	1·204
3·00	2·94	20·15	20·15	79·3	3·82
4·00	3·87	19·5	20·8	91·1	10·84
5·00	4·71	19·9	20·8	94·3	19·37
7·00	6·38	18·3	22·15	96·7	36·0
8·00	6·40	15· 9	24·2	97·1	51·0

(b) 5·14 × 10^{-5}M-*Indium in* HBr.

N′	N	V_o	V	E	q
0·050	0·050	20·0	20·0	3·7	0·0386
0·10	0·10	20·0	20·0	10·0	0·111
0·20	0·20	20·0	20·0	49·9	0·995
0·40	0·40	20·0	20·0	86·4	6·34
0·50	0·50	20·0	20·0	92·9	13·1
0·75	0·73	19·5	20·5	97·8	47·4
1·00	0·975	19·5	20·5	99·1	119
3·00	2·89	19·1	20·9	99·8	459
6·00	4·63	23·6	16·7	99·2	89·1

(c) 1·72 × 10^{-6}M-*Indium in* HI.

N′	N	V_o	V	E	q
0·005	—	19·9	20·1	3·9	0·0406
0·010	—	19·7	20·3	36·1	0·582
0·015	—	19·6	20·4	57·0	1·38
0·020	—	19·8	20·2	72·6	2·70
0·050	0·0498	19·8	20·2	99·0	97·6
0·10	0·10	19·8	20·2	99·7	325
0·15	0·135	19·6	20·4	99·9	1215
0·50	0·49	19·5	20·5	99·9	1190
4·00	3·18	24·8	15·2	99·7	213·5

V. *Furfuraldehyde.*

(a) 7·92 × 10^{-5}M-*Indium in* HCl.

N′	N	V_o	V	E	q
0·10	0·098	19·5	20·4	2·9	0·031
1·00	0·97	19·3	20·5	9·1	0·106
2·00	1·87	18·6	21·3	21·6	0·315
3·00	2·76	18·2	21·7	42·4	0·879
3·76	3·20	16·8	23·2	58·2	1·925
4·86	3·80	14·0	25·6	64·1	3·27
5·66	3·40	6·85	33·15	41·0	3·37

(b) 7·92 × 10^{-5}M-*Indium in* HBr.

N′	N	V_o	V	E	q
0·10	0·0975	19·4	20·5	2·8	0·0304
0·25	0·20	19·45	20·55	20·1	0·266
0·50	0·44	18·8	20·7	37·0	0·648
0·80	0·72	18·8	20·8	61·0	1·73
1·00	0·96	18·8	20·8	77·4	3·79
1·53	1·28	18·2	21·55	89·6	10·2
1·98	1·79	18·15	21·75	96·6	33·6
2·50	2·04	16·8	22·9	97·8	60·2
3·32	2·05	11·85	28·0	91·2	24·5

(c) 7·92 × 10^{-5}M-*Indium in* HI.

N′	N	V_o	V	E	q
0·016	—	19·7	20·2	5·1	0·0548
0·034	—	19·75	20·15	20·0	0·255
0·040	—	19·6	20·1	30·1	0·442
0·060	—	19·65	20·05	63·8	1·80
0·106	0·100	19·6	20·0	92·7	12·9
0·250	0·247	19·4	20·2	99·3	138·6
0·495	0·490	19·35	20·2	~100	1000
1·98	1·95	19·7	20·2	97·1	34·5

VI. *Ethyl acetate.*

(a) 3·30 × 10^{-5}M-*Indium in* HCl.

N′	N	V_o	V	E	q
0·99	0·95 *	18·95	21·05	0·3	0·0034
1·60	1·51	19·0	21·2	1·0	0·00986
2·00	1·88	18·7	21·3	1·8	0·0203
2·13	1·96	18·3	21·8	1·8	0·0214
3·00	2·76	18·4	21·75	5·1	0·0638
4·00	3·56	17·5	22·5	11·7	0·170
4·90	4·20	16·7	23·3	21·4	0·379
5·79	4·52	13·45	26·65	33·4	0·995
7·00	4·02	5·2	34·8	25·7	2·32

(b) 3·30 × 10^{-5}M-*Indium in* HBr.

N′	N	V_o	V	E	q
0·016	0·10 *	18·7	21·3	0·6	0·00631
0·263	0·25	19·1	21·1	4·7	0·0548
0·50	0·467	18·4	21·8	14·8	0·206
1·00	0·92	18·6	21·6	61·3	1·84
1·99	1·79	17·85	22·15	95·2	24·4
3·08	2·61	16·5	23·6	99·3	198
4·02	3·10	13·85	25·95	98·6	136
4·50	2·80	9·25	30·75	92·2	39·2
5·05	2·68	1·6	37·7	32·8	11·5

(c) 3·30 × 10^{-5}M-*Indium in* HCl.

N′	N	V_o	V	E	q
0·017	0·016 *	19·0	21·05	0	0
0·031	0·029	19·0	21·05	0·4	0·00434
0·054	0·051	19·0	20·95	29·2	0·454
0·11	0·10	18·85	21·15	78·8	4·17
0·25	0·23	18·5	21·6	98·3	67·5
0·48	0·45	18·5	21·5	99·8	588
1·91	1·57	15·7	24·2	~100	1828
2·44	1·74	12·0	28·05	97·5	90·7
2·75	1·56	5·0	35·15	52·8	7·87

VII. *Diethyl ether.*

(a) 2·64 × 10^{-4}M-*Indium in* HCl.

N′	N	V_o	V	E	q
4·00	3·46	16·5	22·6	0·7	0·00095
5·00	4·05	15·6	23·7	1·4	0·022
6·00	4·70	13·2	25·5	2·6	0·05

(b) 1·03 × 10^{-5}M-*Indium in* HBr.

N′	N	V_o	V	E	q
0·50	0·465	18·0	21·6	2·0	0·024
1·00	0·91	18·0	22·0	9·6	0·129
2·00	1·80	17·4	22·5	51·6	1·375
3·00	2·58	16·35	23·3	89·3	11·9
4·00	3·26	15·1	24·4	96·5	44·2
5·00	3·43	10·0	29·2	70·9	7·1

(c) 5·4 × 10^{-6}M-*Indium in* HI.

N′	N	V_o	V	E	q
0·10	0·09	17·85	21·95	39·4	0·80
0·25	0·22	17·85	21·8	93·3	17·1
0·49	0·44	17·1	22·6	99·4	211·0
1·55	1·27	16·6	23·2	99·9	1033
2·05	1·60	14·4	25·35	99·3	246
2·50	1·87	12·2	27·4	96·1	54·8
3·15	1·92	6·3	32·8	48·6	4·92
3·50	1·97	6·0	33·2	37·9	3·37

VIII. iso*Pentyl alcohol.*

(a) 1·72 × 10^{-5}M-*Indium in* HCl.

N′	N	V_0	V	E	q
3·00	2·53	21·75	18·25	0	0
4·00	3·31	22·45	17·55	4·2	0·0345
5·00	4·00	23·45	16·55	8·7	0·0672
6·00	4·74	24·8	15·2	15·0	0·108
7·00	5·49	26·4	13·55	19·1	0·121
8·00	6·10	29·1	10·9	30·4	0·164
9·00	6·62	33·3	6·7	52·3	0·221

(b) 1·72 × 10^{-5}M-*Indium in* HBr.

N′	N	V_0	V	E	q
0·50	0·375	20·7	19·3	0	0
1·00	0·724	20·9	19·1	2·4	0·0223
2·00	1·35	21·6	18·4	15·9	0·161
3·00	1·98	22·05	18·0	35·2	0·444
4·00	2·55	22·65	17·4	57·7	1·05
5·00	3·12	23·3	16·7	74·6	2·10
6·00	3·72	24·3	15·7	86·8	4·24
7·00	4·30	25·55	14·45	93·2	7·78
8·00	4·85	27·45	12·55	96·1	11·3
9·00	5·65	29·7	10·3	97·2	12·2

(c) 1·72 × 10^{-5}M-*Indium in* HI.

N′	N	V_0	V	E	q
0·05	0·05	20·6	19·4	2·6	0·0254
0·10	0·095	20·6	19·4	26·3	0·336
0·15	0·135	20·7	19·3	40·9	0·644
0·20	0·17	20·6	19·4	65·0	1·75
0·40	0·325	20·8	19·2	93·1	12·5
0·50	0·425	20·8	19·2	96·2	23·2
1·00	0·74	21·4	18·6	99·2	109
2·00	1·46	22·5	17·5	99·5	155
3·00	2·17	23·4	16·6	99·4	116
4·38	3·20	25·6	14·45	99·4	91·2

IX. iso*Pentyl acetate.*

(a) 4·29 × 10^{-5}M-*Indium in* HCl.

N′	N	V_0	V	E	q
5·00	4·87 *	19·5	20·5	0·2	0·00157
5·95	5·70	19·4	20·6	0·8	0·00856
6·95	6·60	19·1	20·9	4·8	0·055
8·00	7·55	18·85	21·15	6·6	0·079
8·80	8·15	18·4	21·6	12·1	0·161
9·80	8·50	19·0	21·1	11·1	0·1378

(b) 1·72 × 10^{-5}M-*Indium in* HBr.

N′	N	V_0	V	E	q
0·50	0·42 *	20·0	20·0	0	0
1·00	0·98	19·6	20·4	4·8	0·0529
1·50	1·47	19·5	20·5	15·0	0·186
2·00	1·96	19·5	20·4	37·7	0·630
2·50	2·45	19·55	20·45	76·4	2·38
3·00	2·94	19·5	20·5	85·8	6·35
4·00	3·94	19·47	20·53	97·6	42·3
5·00	4·88	19·5	20·5	99·4	167·8
7·10	6·69	19·6	20·4	99·75	414
7·80	7·20	22·4	17·6	99·75	318

(c) 1·72 × 10^{-5}M-*Indium in* HI.

N′	N	V_0	V	E	q
0·030	0·030 *	20·0	20·0	2·5	0·0257
0·050	0·050	20·1	19·9	3·8	0·0386
0·100	0·100	20·1	19·9	14·4	0·166
0·200	0·196	19·55	20·45	56·3	1·35
0·250	0·240	19·6	20·4	74·9	3·10
0·500	0·490	19·6	20·4	97·2	36·7
0·750	0·735	19·7	20·3	99·4	164
5·00	4·54	21·7	18·3	99·9	843
6·00	5·38	29·0	11·0	99·9	468

X. 2 : 2′-*Dichlorodiethyl ether.*

(a) 5·14 × 10^{-5}M-*Indium in* HCl.

N′	N	V_0	V	E	q
5·00	4·72	20·0	20·0	0·5	0·0047
6·00	5·72	20·0	20·0	5·6	0·596
7·00	6·62	20·0	20·0	10·1	0·112
8·00	7·57	20·0	20·0	16·7	0·200
9·00	8·44	20·0	20·0	20·6	0·260
10·0	9·23	20·0	20·0	19·5	0·242

(b) 5·14 × 10^{-5}M-*Indium in* HBr.

N′	N	V_0	V	E	q
0·50	0·494	20·0	20·0	0·4	0·0037
1·00	0·99	20·0	20·0	7·0	0·0753
1·50	1·39	20·0	20·0	17·1	0·207
2·00	1·88	20·0	20·0	40·5	0·680
2·50	2·36	20·0	20·0	57·8	1·37
3·00	2·84	20·0	20·0	80·6	4·15
4·00 †	3·82	20·0	20·0	97·4	37·7
5·00 †	4·71	20·0	20·0	99·2	128
6·00 †	5·69	20·0	20·0	99·6	247

(c) 5·14 × 10^{-5}M-*Indium in* HI.

N′	N	V_0	V	E	q
0·10	0·091	20·0	20·0	0	0
0·143	0·127	20·0	20·0	6·5	0·069
0·25	0·22	20·0	20·0	10·5	0·117
0·30	0·27	20·0	20·0	30·9	0·448
0·358	0·33	20·0	20·0	42·0	0·726
0·40	0·36	20·0	20·0	48·3	0·935
0·60	0·55	20·0	20·0	86·6	5·96
0·75	0·70	20·0	20·0	94·4	16·8
1·00	0·912	20·0	20·0	98·2	53·6
6·00 †	5·35	20·0	20·0	99·6	270

XI. *Di*iso*propyl ether.*

(a) 2·06 × 10^{-5}M-*Indium in* HCl.

N′	N	V_0	V	E	q
5·94	5·82	20·0	20·0	0·2	0·0016
7·95	7·25	18·15	21·55	0·85	0·0102
9·95	6·86	10·75	28·95	2·2	0·0602

(b) 1·17 × 10^{-5}M-*Indium in* HBr.

N′	N	V_0	V	E	q
1·00	0·98	19·6	20·4	0·5	0·0056
2·00	1·95	19·55	20·45	4·8	0·053
3·12	2·94	19·55	20·45	36·1	0·592
4·00	3·65	19·2	20·8	79·8	4·28
5·00	4·80	19·2	20·8	95·0	20·4
6·00	5·56	18·45	21·55	99·0	119
6·72	5·60	15·95	24·0	76·8	4·97
7·80	5·50	7·9	31·1	7·0	0·297

(c) 2·06 × 10^{-5}M-*Indium in* HI.

N′	N	V_0	V	E	q
0·252	0·236	20·0	20·0	19·9	0·249
0·510	0·510	20·0	20·0	71·9	2·56
0·750	0·713	19·45	20·55	95·4	21·8
1·01	0·973	19·25	20·7	99·3	142
2·00	1·96	19·6	20·4	100	2088
4·40	4·04	18·3	21·7	100	2775
4·94 ‡	4·20	14·35	22·25	34·9	18·5
		3·15	—	62·2	151
5·22 ‡	3·72	11·15	19·4	23·7	1·81
		9·45	—	53·7	4·85
5·32 ‡	3·08	9·5	25·4	14·2	0·52
		5·1	—	13·4	0·895
5·50	2·56	9·3	30·5	15·3	0·591

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* These figures are for the final acidity of the halogen acid only and do not include acetic acid formed by hydrolysis.

† At these acidities the organic phase formed the upper layer.

‡ Double entries refer to " light " and " heavy " organic phases respectively.

XII. *Butaldehyde.*

(b) 7·92 × 10^{-5}M-*Indium in* HBr.

N′	N	V	V	E	q
1·01	0·94	17·7	21·2	73·5	3·32
1·43	1·33	17·9	21·5	88·3	9·09
2·03	1·86	17·6	21·9	97·8	54·5

XIII. cyclo*Hexanone.*

(b) 5·14 × 10^{-5}M-*Indium in* HBr.

N′	N	V_0	V	E	q
0·2	—	18·5	21·5	95·9	27·1

XIV. *Miscellaneous solvents.* The values given are for the distribution coefficient (q) between 4N-hydrobromic acid and the organic solvent named, 4 × 10^{-6}M-indium being used.

Solvent	q	Solvent	q
Benzene	0	CCl_4	0
Toluene	0·001	$(CH_2Cl)_2$	0·0055
Xylene	0·004	Chlorobenzene	0·001
n-Hexane	0	Nitromethane	27·5
*cyclo*Hexane	0	Nitrobenzene	51·5
CS_2	0	Benzonitrile	440
$CHCl_3$	0·003		

electrodes were connected to a Mullard potentiometer incorporating a cathode-ray tube, and the dead-stop end-point was used. Direct titration was adopted and the end-point was taken to be that for which the " magic-eye " remained open for an arbitrary length of time, *viz.*, 25 sec. (Mitchell and Smith, " Aquametry," Interscience Publ., New York, 1948).

Anhydrous methanol was prepared by refluxing it over magnesium foil and then distilling it (Weissberger and Proskauer, " Organic Solvents," Oxford, 1935). A standard solution of water was obtained by making up 5·0535 g. of distilled water to 1 l. with this anhydrous methanol. Karl Fischer reagent was supplied by Messrs. B.D.H. Ltd., and was of approximately equivalent strength.

After the Karl Fischer reagent had been standardised against the standard solution of water, a convenient aliquot portion (0·25—2·00 ml.) of the organic phase was discharged into the titration vessel from an accurately calibrated pipette against a counter current of nitrogen which was maintained during the titrations to ensure an inert atmosphere. Replicate analyses had a standard deviation of 1·3%. In the following Table $[H_2O]$ is the concentration of water in moles per l. of organic phase and N′ is the initial normality of halogen acid. The volumes of organic solvent and halogen acid were equal before equilibration.

VI. *Ethyl acetate.*

(*a*) HCl, N′	0·0	0·94	2·88	3·72	5·5	6·4
$[H_2O]$	1·46	1·33	1·10	1·03	0·86	0·89
(*b*) HBr, N′	0·0	0·98	1·87	2·66	3·58	4·45
$[H_2O]$	1·46	1·36	1·28	1·18	1·12	1·20

VII. *Diethyl ether.*

(*a*) HCl, N′	0·0	0·94	1·89	2·88	3·72	4·61	5·54	7·77
$[H_2O]$	0·46	0·44	0·39	0·35	0·31	0·28	0·24	0·19
(*b*) HBr, N′	0·0	0·98	1·87	2·66	3·57	4·45	5·35	
$[H_2O]$	0·46	0·41	0·38	0·34	0·32	0·29	0·28	

VIII. iso*Pentyl alcohol.*

(*a*) HCl, N′	0·0	1·90	3·72	5·54	7·58	8·93
$[H_2O]$	4·5	5·16	7·34	10·4	14·8	19·5
(*b*) HBr, N′	0·0	1·87	4·45	5·35	7·66	
$[H_2O]$	4·52	6·11	10·0	12·0	18·4	

IX. iso*Pentyl acetate.*

(*a*) HCl, N′	0·0	0·94	2·88	4·61	6·40	7·58	9·02
$[H_2O]$	—	0·57	0·48	0·38	0·34	0·32	0·58
(*b*) HBr, N′	0·0	0·98	2·66	4·45	5·35	6·02	7·66
$[H_2O]$	0·61	0·57	0·48	0·44	0·54	0·78	7·15

XI. *Di*iso*propyl ether.*

(*a*) HCl, N′	0·0	0·94	2·88	4·61	7·58	
$[H_2O]$	0·208	0·196	0·170	0·140	0·101	
(*b*) HBr, N′	0·0	0·98	1·87	3·57	5·37	7·66
$[H_2O]$	0·208	0·201	0·188	0·148	0·124	0·109

DISCUSSION

Comparison with Previous Work.—Ato's results (*loc. cit.*) for 10^{-2}M-indium in the ether–hydrochloric acid system agree satisfactorily with ours so far as direct comparison is possible. There is also good agreement with the data of Hudgens and Nelson (*loc. cit.*) who worked with indium concentrations down to 10^{-3}M in the *iso*propyl ether–hydrobromic acid system. Detailed comparison with Wada and Ishii's results (*loc. cit.*) for the extraction of $4{\cdot}4 \times 10^{-2}$M-indium into diethyl ether is not possible as the Japanese workers do not record values for distribution ratios or equilibrium acidities, but the present results suggest that at low acidities the extraction of indium is more effective at the concentration level of $\sim 10^{-5}$M we have employed. However the values obtained in the present work are consistently lower than those reported by Bock, Kusche, and Bock (*loc. cit.*) who used 10^{-1}M-indium, and the amount of indium extracted from hydrobromic acid into ether appears to increase with indium concentration (cf. Part IV).

The effect of changes in acidity on the distribution of indium halides is conveniently displayed by plotting the logarithm of the distribution ratio, q, against the logarithm of the acidity, N, of the aqueous phase after equilibration. For extraction from hydriodic acid, all the solvents studied gave curves of a similar form (Fig. 1). Log q first increases almost linearly with log [HI], then passes through a fairly sharp maximum, and finally falls off more or less rapidly.

Families of similar curves for extraction from hydrobromic acid are shown in Fig. 2. Those representing extraction from hydrochloric acid (Fig. 3) have rather steeper slopes than those shown in Figs. 1 and 2, particularly for extraction into the " less efficient " solvents, *i.e.*, solvents which effect appreciable extraction only at high acidities.

Form of Distribution Curves.—A complete discussion, in quantitative terms, of the distribution for all the systems investigated is impossible, partly because the ionic strength in the aqueous phase was not constant (see p. 1947) and partly because increasing miscibility of the phases with increasing acidity entails many complications. But, provided that the concentration of indium in the system is small compared to that of all other species (as in the experiments under consideration), its distribution should not materially affect that of any other species which undergo partition, *e.g.* water, organic solvent, or halogen acid; the value of the distribution coefficient should, in turn, be determined essentially by the composition of the organic and the aqueous phase. Neglecting for the moment the effect of any changes in phase compositions on the partition coefficients and stability constants of the various species present in equilibrium, the dependence of q on the concentration variables in the aqueous phase follows from the general treatment proposed in Part I. At the low indium concentrations ($\sim 10^{-5}$M) used in the present work it can reasonably be assumed that no polynuclear species are present in the aqueous or the organic phases (cf. Parts III and IV), and the average composition of the complex species in the organic and aqueous phases may be represented by $H_{\bar{\mathbf{h}}}InX_{\bar{\mathbf{n}}}$ and $H_{\bar{h}}InX_{\bar{n}}$ respectively, where X = Cl, Br, or I, and $\bar{h}$ and $\bar{n}$ are " ligand numbers " giving the average number of hydrogen or halide ions respectively attached to each atom of indium. Ligand numbers referring to the organic phase are distinguished by heavy (Clarendon) type from those referring to the aqueous phase which are in italics.

Equation (1) may now be written

$$q = [H_{\bar{\mathbf{h}}}In\ X_{\bar{\mathbf{n}}}]_0/[H_{\bar{h}}InX_{\bar{n}}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and, introducing definitions for (stoicheiometric) partition coefficients and stability constants, *viz.*,

$$p_{h1n} = [H_hInX_n]_0/[H_hInX_n] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\beta_{h1n} = [H_hInX_n]/[H^+]^h[In^{3+}][X^-]^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

we obtain

$$\log q = \log p_{\bar{\mathbf{h}}1\bar{\mathbf{n}}}\ \beta_{\bar{\mathbf{h}}1\bar{\mathbf{n}}}/\beta_{\bar{h}1\bar{n}} + (\bar{\mathbf{h}} - \bar{h}) \log [H^+] + (\bar{\mathbf{n}} - \bar{n}) \log [X^-] \quad . \quad (5)$$

In this treatment (cf. Part I) it is assumed that the degree of solvation and hydration does not change over the range of acid and halide-ion concentrations studied, and that activity coefficients are constant.

In a solution where the strong halogen acid HX is the only source of hydrogen and

FIG. 1.

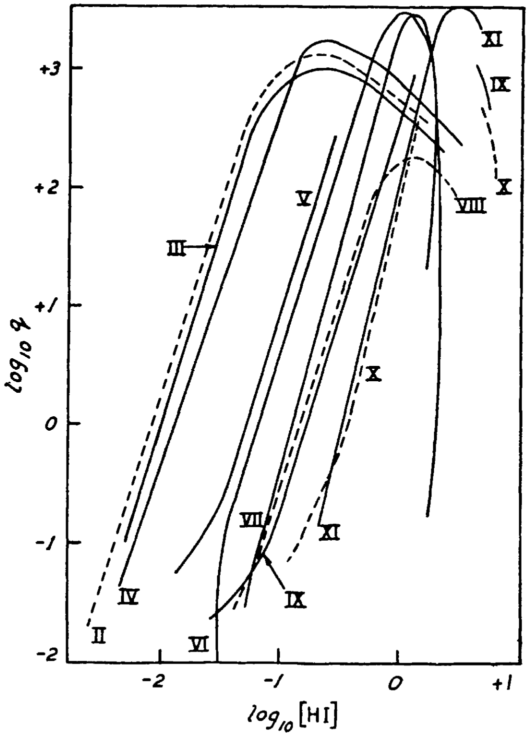


FIG. 2

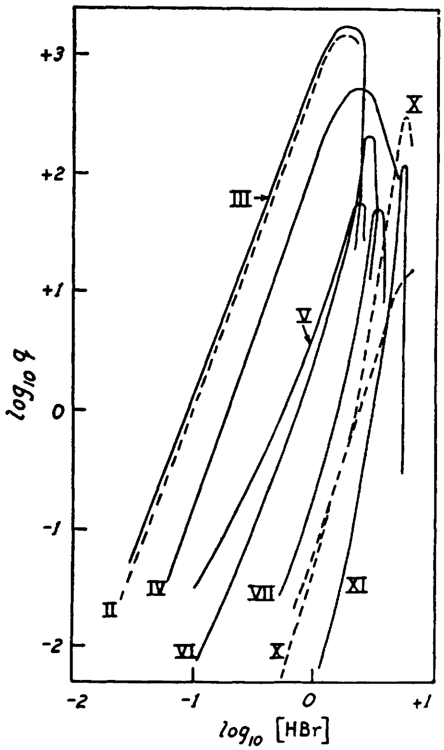
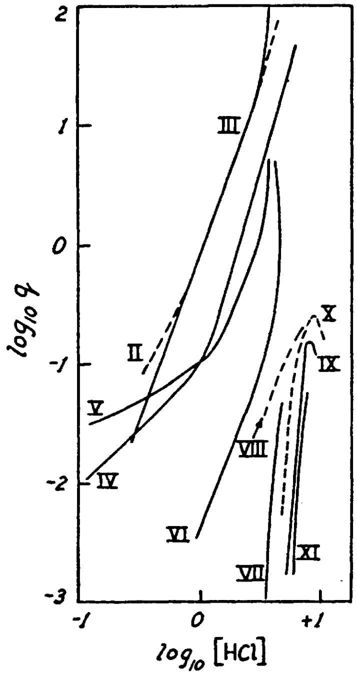


FIG. 3.



The extraction of indium from (FIG. 1) *hydriodic acid,* (FIG. 2) *hydrobromic acid,* (FIG. 3) *hydrochloric acid. The variation of distribution ratios with equilibrium acidities.*

halide ions, and where its concentration C_{HX} is greatly in excess of the total concentration C_{In} of indium we have $[\mathrm{H}^+] = [\mathrm{X}^-] = C_{\mathrm{HX}}$, so that equation (5) reduces to :

$$\log q = \text{constant} + \{(\bar{\mathbf{h}} - \bar{h}) + (\bar{\mathbf{n}} - \bar{n})\}\log C_{\mathrm{HX}}$$

and

$$(\partial \log q/\partial \log C_{\mathrm{HX}}) = (\bar{\mathbf{h}} - \bar{h}) + (\bar{\mathbf{n}} - \bar{n}) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

There is no evidence for higher halide complexes than InX_4^- in aqueous solutions (Carleson and Irving, *J.*, 1954, **4390**, and refs. therein) so that the maximum value of $\bar{n}$ is 4 in these equations.

If InX_3 were the sole metallic species in the organic phase, then

$$\lim_{C_{\mathrm{HX}} \to 0} (\partial \log q/\partial \log C_{\mathrm{HX}}) = 3$$

and

$$\lim_{C_{\mathrm{HX}} \to \infty} (\partial \log q/\partial \log C_{\mathrm{HX}}) = -2$$

and at moderate acidities

$$(\partial \log q/\partial \log C_{\mathrm{HX}}) = (3 - \bar{n}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if the reasonable assumption be made that $\bar{h} \approx 0$. At present there is no evidence that metal acido-complexes are not strong acids (cf. for ferrocyanic acid, Nekrassov and Zotov, *J. Appl. Chem. U.S.S.R.*, 1941, **14**, 264; *Chem. Abs.*, 1942, **36**, 1834). Similarly, if HInX_4 were the sole species in the organic phase, then

$$\lim_{C_{\mathrm{HX}} \to 0} (\partial \log q/\partial \log C_{\mathrm{HX}}) = 5; \quad \lim_{C_{\mathrm{HX}} \to \infty} (\partial \log q/\partial \log C_{\mathrm{HX}}) = 0$$

and at moderate acidities

$$(\partial \log q/\partial \log C_{\mathrm{HX}}) = (5 - \bar{n}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For a given halogen acid, HX, at any arbitrary concentration C_{HX}, $[\mathrm{X}^-]$ is fixed (provided $C_{\mathrm{HX}} \gg C_{\mathrm{In}}$) so that $\bar{n}$ (which is a function only of $[\mathrm{X}^-]$ and the various stability constants, β) is also fixed. Hence the gradient of all curves of log q against log C_{HX} should be the same for a given value of C_{HX}. But since $\bar{n}$ increases with C_{HX}, the slope should decrease as the acid concentration is increased and we should expect for different solvents a family of curves, convex towards the concentration axis and differing only by a vertical displacement corresponding to changes in the values of log p_{h1n} for the different solvents. Consider finally the case where InX_3 and HInX_4 undergo partition simultaneously. At low values of C_{HX} where the degree of complex formation in the indium–halide ion system is low, InX_3 will predominate in the organic phase, irrespective of the relative magnitudes of the partition coefficients p_{013} and p_{114}. Thus the gradient $\partial \log q/\partial \log C_{\mathrm{HX}}$ approaches the value 3 as C_{HX} approaches zero; but since the amount of the complex InX_4^- formed increases in proportion to $[\mathrm{X}^-]^4$, while that of InX_3 increases only in proportion to $[\mathrm{X}^-]^3$, $\partial \log q/\partial \log C_{\mathrm{HX}}$ will tend to the value $(5 - \bar{n})$ as C_{HX} increases. If, however, $p_{114} \gg p_{013}$ (*i.e.*, the partition coefficient for the acido-complex HInX_4 is much larger than that of the neutral species InX_3), $\partial \log q/\partial \log C_{\mathrm{HX}}$ will approximate to $(5 - \bar{n})$ for all values of C_{HX}. If, on the contrary, $p_{114} \ll p_{013}$, $\partial \log q/\partial \log C_{\mathrm{HX}}$ will approximate to $(3 - \bar{n})$ at low values of C_{HX} (where $\bar{n}$ is also low), but to $(5 - \bar{n})$ at high values of C_{HX} (where the value of $\bar{n}$ will also be larger). Changes in the gradient of the plot of log q against log C_{HX} will therefore be less than would have been the case had either InX_3 or HInX_4 been the sole species extracted; indeed the graph may appear to be effectively linear over a limited concentration range (cf. Figs. 1, 2, and 3), or even concave to the concentration axis.

The Experimentally Determined Distribution Curves.—In the main, all the experimental results may be interpreted on the basis of the foregoing discussion though the phenomena are clearly more complex with hydrochloric acid than with the other halogen acids. The discussion will be limited in the first instance to positive values of $\partial \log q/\partial \log C_{HX}$. For the iodide system (Fig. 1) the slope of plots of log q against log C_{HI} approximate to 4 for all solvents studied; for the bromide system (Fig. 2) the slopes of plots of log q against log C_{HBr} approximate to 3 for all solvents. For each acid, the similar value of the slope at corresponding acidities supports the hypothesis that the same type of predominating species is extracted irrespective of the solvent. The gradient of 4 found for the iodide system excludes the possibility that InI_3 is the predominant species in the organic phase [cf. equation (7)], and points towards $HInI_4$. Indeed a detailed analysis of the system indium bromide–hydrobromic acid–*iso*butyl methyl ketone (Parts III and IV) establishes that the predominant species extracted from acid solutions is $HInBr_4$,aq. If it is assumed that an acido-complex $HInX_4$ is the predominant species extracted from hydriodic or hydrobromic acid by all solvents, then the mean value of $\bar{n}$ is of the order of 1 and 2 respectively in the concentration regions studied [cf. equation (8)]. It is apparent from the known stability constants of indium halide ion complexes (Carleson and Irving, *loc. cit.*) that the iodide ion complexes are less stable than those with bromide ions and these values for $\bar{n}$ appear quite reasonable (cf. Part IV).

At macro-concentrations of indium it has been shown by analysis that $HInCl_4$ is the predominant species extracted from hydrochloric acid into *iso*butyl methyl ketone (Irving and Rossotti, unpublished observation). $HInBr_4$,aq. is known to be extracted from hydrobromic acid into diethyl ether or *iso*butyl methyl ketone (Part IV). The presence of the $InBr_4^-$ ion in such organic extracts is supported by a study of their Raman spectra (Woodward and Bill, unpublished work). Indeed there is a wealth of data pointing to the predominant extraction of acido-complexes, HMX_4,aq., into aliphatic ethers from acid solutions of tervalent halides at macro-concentrations, *e.g.*, for Fe^{3+} (Axelrod and Swift, *J. Amer. Chem. Soc.*, 1940, **62**, 33; Nachtrieb and Fryxell, *ibid.*, 1948, **70**, 3552; Bock, Kusche, and Bock, *loc. cit.*), for Au^{3+} (Mylius, *Z. anorg. Chem.*, 1911, **70**, 203; Bock, Kusche, and Bock, *loc. cit.*; Haas, Ph.D. Thesis, Chicago, 1950), for Ga^{3+} (Nachtrieb and Fryxell, *J. Amer. Chem. Soc.*, 1949, **71**, 4035; Bock, Kusche, and Bock, *loc. cit.*), and for In^{3+} and Tl^{3+} (Bock, Kusche, and Bock, *loc. cit.*). There is also evidence that non-acidic species, MX_3, will partition in certain circumstances (Part III, and refs. therein), but at macro-concentrations the assumption that the acido-complex, $HInX_4$,aq., is the predominant species extractable from halogen acids may be considered established.

Individual distribution curves (Figs. 1, 2, and 3) are surprisingly linear in those portions where the gradient $\partial \log q/\partial \log C_{HX}$ is positive. It has been pointed out (p. 1955) that the co-extraction of InX_3 with $HInX_4$ provides a mechanism for counteracting the predicted convexity of such distribution curves towards the concentration axis. Another factor is that the dependence of phase miscibility on C_{HX} (p. 1964) limits variations in this term to little more than one logarithmic unit even in favourable cases and curvature of the distribution curves may not become apparent over so limited a range.

On changing from one solvent to another into which extraction occurs less readily it is necessary to proceed to higher acidities (and consequently to higher values of $\bar{n}$) to achieve a given value of q. Hence a somewhat lower value of the gradient [$= (5 - \bar{n})$ by equation (8)] would be expected in such solvents; the reverse behaviour is generally found. Moreover, slopes greater than 5 are found in extractions from hydrochloric acid, especially with the less efficient solvents with which very high acidities (4N to 9N) are required to yield appreciable extraction. Such high slopes cannot be explained in terms of the simplified theory put forward above (cf. Part I) and it is evident that a number of complicating factors must be considered.

In deriving equation (5) it was postulated that concentrations could be used in place of activities; in the present experiments it was impossible to control the ionic strength. The activity coefficients of the halogen acids increase very markedly with concentration (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1950) and a partial correction may be applied by plotting log q against the logarithm of the activity of the acid used. A more serious difficulty in applying equation (5) to the results of the present experiments is that it refers strictly to what we have termed "ideal" extraction systems (Part I), *i.e.*, those in which the nature and composition of the phases does not change with changes in acid concentration so that (stoicheiometric) partition coefficients and stability constants may be considered truly constant over the whole range of experimental conditions. This will certainly not be valid for solvents whose miscibility with water is strongly dependent on acid concentration (p. 1964), and equation (5) will then become less applicable as the acid concentration is increased, irrespective of the solvent, and still less applicable for the less efficient solvents. As the aqueous phase becomes increasingly organic in character as complete miscibility is approached, stability constants and the extent of the formation of extractable species are likely to increase. But if the dissociation of hydrogen and halide ions also increases appreciably, competition of indium and of hydrogen ions for halide ions will tend to lower $\bar{n}$.

In deducing equation (5) it was further assumed that the extent of solvation of the extracted species does not vary with acid concentration, and that the activity of water and of organic solvent in the two phases is likewise constant. Although this condition may be met when tracer concentrations of metal are used and a solvent is chosen whose miscibility with the aqueous phase does not change with acid concentration (Part IV), conditions are certainly more complex in many of the present experiments. It is known that $HInBr_4$ is accompanied by 10 molecules of water when extracted into diethyl ether (Part IV); if this water is closely associated with the complex the tenth power of the activity of the water should enter into the equilibrium conditions. But as the concentration of hydrogen halide in the aqueous phase is increased, the activity of water there is decreased, some water is transported into the organic phase by the acido-complex as it undergoes partition, and organic solvent passes into the aqueous phase. For such reasons no simple treatment of distribution at high acidities, or into highly miscible solvents, can be expected.

Retrograde Extraction.—The distribution curves for the indium halides frequently exhibit maxima (Figs. 1, 2, and 3), and at sufficiently high acidities the values of the gradient, $\partial \log q/\partial \log C_{HX}$, become negative. If the species which undergoes partition is the highest complex formed in the aqueous phase, its partition coefficient is given by the limiting value of the distribution ratio, q, as the free ligand concentration is indefinitely increased (Part I), and many examples are afforded by the extraction of inner complexes of metals with organic reagents (cf. Dyrssen, *Svensk Kem. Tidskr.*, 1953, **65**, **43**; Dyrssen and Dahlberg, *Acta Chem. Scand.*, 1953, **7**, 1186). In the absence of changes in phase composition, negative values of $\partial \log q/\partial \log C_{HX}$ then indicate the formation of higher complexes in the aqueous phase than that which undergoes partition (Part I). Thus in the system ferric thiocyanate–diethyl ether, the occurrence of a maximum value of q was correlated with a maximum in the fraction of iron present as the extractable species $Fe(CNS)_3$, higher anionic species being formed increasingly at higher concentrations of thiocyanate ion (Macdonald, Mitchell, and Mitchell, *J.*, 1951, 1574). However, with indium systems there is no evidence for higher complexes than InX_4^- in aqueous solutions (Carleson and Irving, *loc. cit.*). Moreover the negative values of the gradient are extremely large and even approach infinity, so that the decrease in extraction at high acidities requires some explanation other than a shift in the step-equilibria towards higher complexes than that extracted.

It appears that decreases in distribution coefficient always coincide with gross changes in phase volumes on equilibration in the present experiments. Data for the extraction of gallium, indium, and thallium halides into diethyl ether (Irving and Rossotti, *loc. cit.*) indicate that the retrograde extraction observed with these metals into any one of the halogen acids takes place at the same acidity and is independent of the nature of the metal. The phenomenon is thus specific for each acid–solvent combination and may be correlated with the rapid decrease in partition coefficients with approaching complete phase miscibility (Part I). Metzler and Myers (*J. Amer. Chem. Soc.*, 1950, **72**, 3776) correlated the maximum in the extraction of ferric chloride from hydrochloric acid into ethers with the miscibility of aqueous and organic phases in these systems.

Curves of Percentage Extraction.—For all the solvents studied in detail the percentage of indium extracted increases at first with the increasing initial concentration of acid, N', in the aqueous phase. Such increases in E are due, in the first instance, to increases in the distribution ratio, q, which in turn can be related to the increasing formation in the aqueous phase of the particular species which undergoes partition (cf. equation 13 of Part I). At higher acidities the percentage extraction, defined by equation (2), usually passes through a maximum and eventually decreases. The percentage of indium extracted from hydrochloric acid is shown in Fig. 4. Even from the best solvents (methyl propyl and methyl *iso*propyl ketone), quantitative extraction is not attained until acid of initial normality 5N is used, while with the less efficient solvents (2 : 2′-dichlorodiethyl and di*iso*propyl ether) the maximum extraction of a few percent is not attained until acid of strength ~9N is used. The corresponding curves for extraction from hydrobromic acid (Fig. 5) are generally similar but the maximum extraction occurs at appreciably lower initial acidities

Fig. 4.

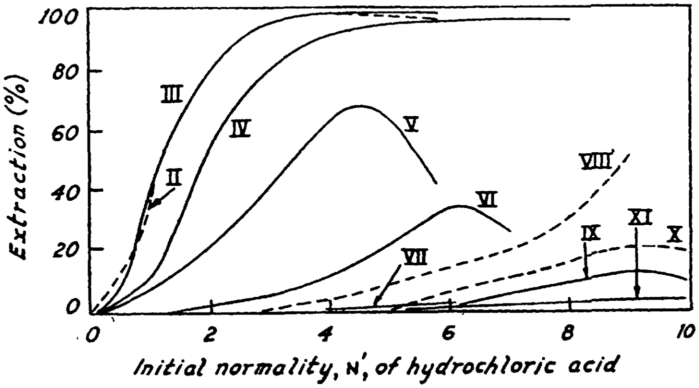
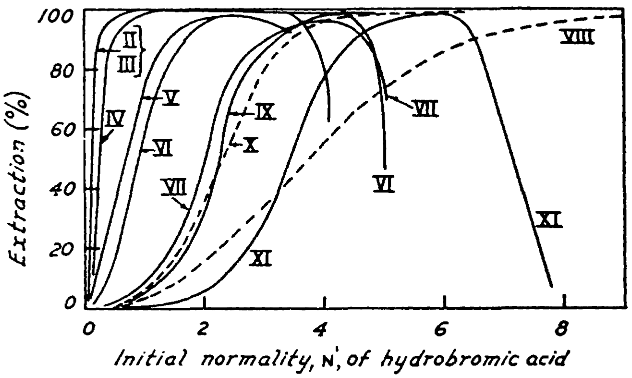
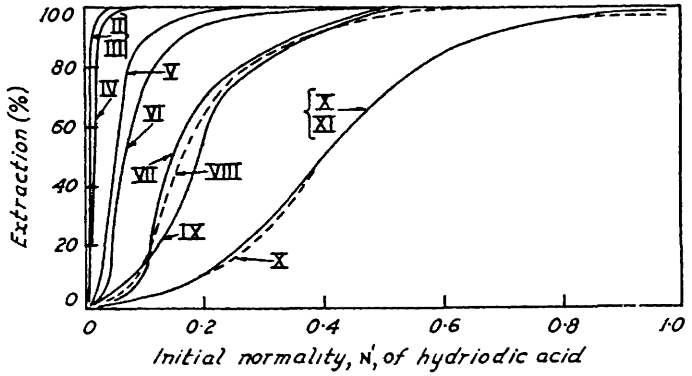


Fig. 5.



The percentage of indium extracted from (Fig. 4) *hydrochloric acid,* (Fig. 5) *hydrobromic acid,* (Fig. 6) *hydriodic acid by an equal volume of organic solvent.*

Fig. 6.



(1—6N). In extractions from hydriodic acid (Fig. 6; note the greatly expanded scale of initial normalities) this trend is further accentuated and maximum extraction is achieved with all solvents below N′ = 1, and for the most efficient solvents at an initial concentration of no more than 0·1N-hydriodic acid. In all these extractions, both the distribution ratio, q, and the ratio of phase volumes at equilibrium, R, depend on the acidity at equilibrium, N. Hence the sign of the gradient $\partial E/\partial N$ will depend upon the signs and relative magnitudes of both $\partial R/\partial N$ and $\partial q/\partial N$, and the present results illustrate the wide variety of behaviour which may be expected in different systems. With *iso*pentyl alcohol, E increases monotonically with acidity for each halogen acid because there is a concomitant increase in R and an increase in q with increasing acidity. The situation is analogous to the extraction of nitrates into diethyl ether from nitric acid where V_0 also increases at the expense of V on equilibration, and where no retrograde extraction is observed. In the extraction of indium from hydrochloric acid by ethyl acetate or by furfuraldehyde the decrease in R soon outweighs the increase in q, and E passes through its maximum value at less than 100% extraction. In these two systems q may still be capable of further increase although the acidity of the aqueous phase after equilibration has reached the largest value realisable under the present experimental conditions. This is presumably because the nature of the phases is still being modified in a manner favourable to partition. The converse behaviour, *viz.*, a sharp decrease in the value of q, will result when the phase compositions become less favourable to partition. The effect on the value of E will be greatest at high initial acidities where q is approaching a limiting value owing to the approaching identity of phases, and where the phase ratio, R, is large. In the *iso*pentyl alcohol–hydriodic acid system, q passes through a maximum (Fig. 1) even though the equilibrium acidity, N, is still increasing; however, as the rate of increase in R is comparatively small, the effect on E is scarcely perceptible at the highest acid concentrations examined.

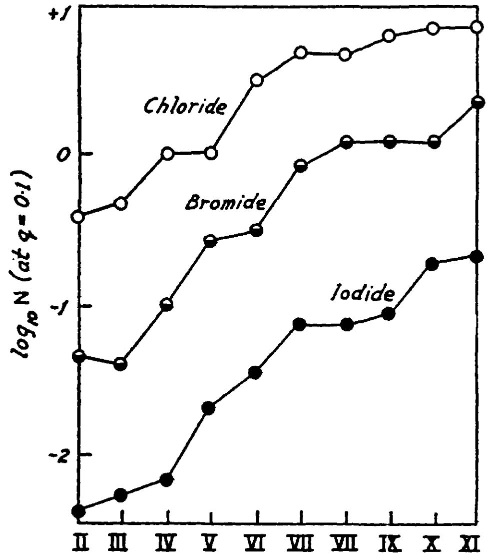


FIG. 7. *The order of solvent efficiency.* (*The organic solvents denoted by Roman numerals are named in Table* 2.)

The Order of Solvent Efficiency.—The concentration of halogen acid required in the aqueous phase to afford an arbitrary distribution of metal may be used as a measure of the relative efficiency of the different solvents. As an empirical basis for such comparisons values of log N corresponding to log $q = -1$ were read off from plots (Figs. 1, 2, and 3). This choice of $q = 0{\cdot}1$ was made to avoid long extrapolations, but the same conclusions could be drawn from values of log q corresponding to, *e.g.*, log $N = 0$. The values of log N are plotted as ordinates in Fig. 7, and the different solvents have been arranged in a monotonic series which holds, with but minor modifications, for each halogen acid. The order of decreasing efficiency is methyl propyl or methyl *iso*propyl ketone > *iso*butyl methyl ketone > furfuradehyde > ethyl acetate > diethyl ether > *iso*pentyl alcohol > *iso*pentyl acetate > 2 : 2′-dichlorodiethyl ether > di*iso*propyl ether. For any one solvent the extraction efficiency decreases to much the same extent on replacement of hydriodic acid by hydrobromic acid, or of hydrobromic acid by hydrochloric acid. Assuming the predominant species extracted to be $HInX_4$,aq. in every case, we have (cf. Part I)

$$q = p_{114}\alpha_4 K^{H}[H^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where p_{114} is the partition coefficient of the species $HInX_4$, $K^{H} = [HInX_4]/[H^+][InX_4^-]$ and α_4 is the degree of formation of the species InX_4^- in the aqueous phase. Here

$$\left.\begin{aligned} \alpha_n &= \beta_{01n}[X^-]^n / \sum_{n=0}^{n=4} \beta_{01n}[X^-]^n \\ \text{and} \qquad \beta_{01n} &= [InX_n]/[In^{3+}][X^-]^n \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

At any arbitrary value of N (and thus at an arbitrary value of $[X^-]$ and $[H^+]$), α_4 may reasonably be assumed to decrease in the order chloride > bromide > iodide, from what is known of the stability constants in the indium–halide systems (Carleson and Irving, *loc. cit.*). The experiments have shown that q increases in the order chloride < bromide < iodide, so since $K^{H}[H^+]$ will be constant (unless the effects of small amounts of organic solvents in the aqueous phase introduce quite unexpected anomalies), the magnitude of the partition coefficients, p_{114}, for the three halide complexes will increase in the same order.

It is often possible to arrive at an approximate value for the partition coefficient of a sparingly soluble neutral species (*e.g.*, iodine, sulphur hexafluoride) by independent measurements of its solubility in water and in an organic solvent. Table 1 shows the ratio of the solubility of an indium halide in an organic solvent to its solubility in water, calculated from measurements by Ensolin and Dreyer (*Z. anorg. Chem.*, 1942, **249**, 119) and Ensolin and Lessman (*ibid.*, 1947, **254**, 92). These are seen to decrease in the order iodide > bromide > chloride. The behaviour of acetone is the sole exception amongst the 14 solvents studied. If the indium is assumed to exist as the trihalide in the organic phase and as mononuclear species in the aqueous phase, then distribution ratios and partition coefficients are related (Part I) by the equation

$$q = \alpha_3 p_{013} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $p_{013} = [InX_3]_0/[InX_3]$, and α_3 is defined by equation (10). From the known molar solubilities of indium trichloride, tribromide, and tri-iodide in water (5·73, 6·74, and 6·36 moles/l.; Ensolin and Dreyer, *loc. cit.*) and the known stability constants (Carleson and Irving, *loc. cit.*) values of α_3, the degree of formation of the trihalide complexes in the saturated aqueous solution, can be estimated as 0·75, 0·7, and 0·65 respectively, so that the magnitudes of the partition coefficients for InX_3 must increase in the order chloride < bromide < iodide.

TABLE 1. *The ratio of the solubilities of indium halides in various organic solvents to their solubilities in water* (*at* 22°).

Solvent	$InCl_3$	$InBr_3$	InI_3	Solvent	$InCl_3$	$InBr_3$	InI_3
Chloroform	0·023	0·039	0·97	Diethyl ether	0·523	0·887	0·921
Pentanol	0·344	0·612	0·640	Acetone	0·570	0·898	0·807
Pentyl acetate	0·393	0·697	0·795	Ethyl alcohol	0·59	0·69	—
Ethyl acetate	0·573	0·745	0·843				

Relation between the Efficiency of a Solvent as an Extracting Agent and its Physical Properties.—The energy needed to transfer a substance across a phase boundary may be regarded as arising from the greater stability of the (solvated) species in the organic phase compared with that in the aqueous phase (McKay, A.E.C.U. 2246). The existence of an order of solvents which alters very little with the nature of the material extracted would suggest that such stability factors depend more on the properties of the two phases than on the intrinsic nature of the solute.

The ten solvents investigated in detail and those other solvents which were found extract indium efficiently, *viz.*, butaldehyde, *cyclo*hexanone, nitromethane, and benzonitrile, are all electron donors, and it is of interest that the donor atom need not be oxygen. Previous workers on solvent extraction have adopted the viewpoint that the order of extractability by a series of solvents is that of their power to form hydrogen bonds (Katzin and Ferraro, *J. Amer. Chem. Soc.*, 1953, **75**, 3821; Wylie, *J.*, 1951, 1474). The order of the strengths of hydrogen bonds formed between deuterated methanol and organic solvents is reported as alcohols > ethers > ketones > aldehydes > esters > nitro-compounds (Stanford and Gordy, *J. Chem. Phys.*, 1940, **8**, 170). For the particular solvents investigated in detail in this paper, their order is diethyl ether > di*iso*propyl ether > 2 : 2′-dichlorodiethyl ether and pentyl acetate > ethyl acetate > furfuraldehyde > *iso*butyl methyl ketone. Clearly the order of solvents now found experimentally cannot be explained in terms only of the Gordy index, $\Delta\nu$, of hydrogen-bond formation. Wiberley, Clark, and Bassett (U.S. Atomic Energy Commission Declassified Reports, New York Operations, 609), by using a spectroscopic technique similar to that of Gordy, found little correlation between the capacity of amines and ethers to accept protons and their behaviour as solvents, although it was clear that an electron donor–acceptor mechanism is involved. Gordy and Stanford (*loc. cit.*) observed little correlation between dipole moment, μ, and $\Delta\nu$. The former must be a relevant factor in the solvation of the species which is extracted and so in the extractive efficiency of a solvent. Acido-species of the type HMX_4,aq., probably exist as ion pairs and act as strong electrolytes (Part IV). An ion pair will be the more stable in a medium of low dielectric constant, but the free energy of transfer of the species undergoing partition will be lower the greater the dielectric constant of the organic phase. Solvents which extract water most readily are also found to extract inorganic salts most readily, and this may be correlated with the increasing dielectric constant of the organic phase with increasing water content.

It has frequently been observed that the lowest member of a homologous series is the most efficient extractant (Wylie, *loc. cit.*; Templeton and Hall, *J. Phys. Colloid Sci.*, 1947, **51**, 1441; Warner, *Austral. J. Appl. Sci.*, 1952, **3**, 156) and such an effect is substantiated by the present results. On steric grounds, the smaller the molecule of the solvent, the more readily should it be able to become attached to the species which is extracted. However the greater effectiveness of the lowest homologue may be due to any one or more of a number of causes, since almost any property which may be considered relevant to solvent extraction (cf. Table 2) generally has its most favourable value for the lowest homologue.

TABLE 2. *The solvents arranged in order of decreasing efficiency, and values of some of their physical constants.**

Number	Solvent	$\Delta\nu$	μ	ε	S	$10^3(MV)^{-1}$
II	Methyl propyl ketone	—	2·70	15·4	1·62	9·4
III	Methyl *iso*propyl ketone	—	2·76	—	1·94	9·4
IV	Methyl *iso*butyl ketone	77	2·79	13·1	1·25	7·8
V	Furfuraldehyde	70	3·57	42	3·22	12·0
VI	Ethyl acetate	84	1·82	6·02	1·5	10·2
VII	Diethyl ether	130	1·17	4·33	0·52	9·6
VIII	*iso*Pentyl alcohol	—	1·82	5·7	4·34	9·2
IX	*iso*Pentyl acetate	90	1·82	4·63	0·49	6·8
X	2 : 2′-Dichlorodiethyl ether	84	2·58	21·2	0·19	8·6
XI	Di*iso*propyl ether	123	1·2	3·88	0·25	7·1

* The frequency shift, $\Delta\nu$, is proportional to the strength of the hydrogen bond (Gordy and Stanford, *loc. cit.*). Values of μ refer to solutions in benzene at 20° (Wesson, "Tables of Electric Dipole Moments," Massachusetts Inst. Technology, 1948). The dielectric constants, ε, are taken from Maryott and Smith's "Tables of Dielectric Constants of Pure Liquids," Nat. Bur. Standards Circular 514, 1951. Molar solubilities, S, of water in the organic solvents, and reciprocal molar volumes $(MV)^{-1}$, at 20° are calculated from data in Mellan's "Industrial Solvents," Reinhold Publ. Corp., New York, 1950.

The substantially identical extraction efficiency of the metameric methyl propyl and methyl *iso*propyl ketones is not surprising as their physical properties are much the same, and the branched-chain isomer is unlikely to offer much greater steric hindrance to solvation.

Table 2 presents values for most of the physical properties which have been considered relevant to discussions of solvent extraction. The solvents are arranged in order of decreasing efficiency for the extraction of indium halides (cf. Fig. 7). While detailed correlation is impossible, most of these physical properties have large values for the best extracting solvents. Conversely, the hydrocarbons, and the other less efficient solvents which were not studied in great detail, have low values of $\Delta\nu$ (where they have been measured), low values of ε, and low or zero values of μ and S.

General " orders of solvents " have been proposed by several workers in the field of chromatography (Trappe, *Biochem. Z.*, 1940, **305**, 150; Lacourt, Sommereyns, Geyndt, and Jacquet, *Mikrochem.*, 1951, **36**, 117; Lederer and Lederer, " Chromatography," Elsevier, London, 1953). While a completely general order cannot be expected (Part I) it is of interest to compare the present results with those for the extraction of other inorganic salts. In Table 3 the solvents used in the present work are again designated by Roman numerals, and since preliminary experiments indicate that *cyclo*hexanone is more efficient than the other ketones it is included as the first member of the list. Arabic numerals in the Table refer to the order of solvent efficiency deduced from measurements by other workers. Wherever possible the order of solvents has been assigned on the basis of distribution ratios measured at a given acidity. In other cases it has been necessary to use reported values for percentage extractions, although such data are not strictly comparable because of different volume changes on equilibration. For these reasons no detailed evaluation of the results, *e.g.*, by statistical ranking methods, is justifiable; but it seems certain that the solvent order derived from the present experimental studies has some measure of generality and could be used as a guide to the choice of solvent, at least in the extraction of similar inorganic complexes.

TABLE 3. *The correlation of solvent orders.*

System	Ref.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
In–HCl	*a*	1	2	3	4	5	6	7	8	9	10	11
In–HBr	*a*	2	1	3	4	5	6	7	8	9	10	11
In–HI	*a*	1	2	3	4	5	6	7	8	9	10	11
In–HCl	*b*	1	—	—	3	2	—	4	—	5	—	—
Ga–HCl	*c*	—	4	—	1	—	3	2	5	6	7	8
Ga–HBr	*c*	—	1	—	2	—	5	3	6	—	—	4
Ga–HI	*c*	—	1	—	2	—	3	4	—	—	—	—
Fe–HCl	*d*	1	—	—	—	—	2	3	4	—	—	—
Fe–HCl	*e*	—	—	—	—	—	—	1	—	—	2	3
Fe–HBr	*f*	—	—	—	1	—	2	3	—	—	—	4
Au–HBr	*f*	—	—	—	1	—	2	3	—	—	—	4
Pb–HI	*g*	—	—	1	2	—	3	—	—	—	—	—
HNO_3	*h*	—	1	—	2	—	—	3	—	—	5	4
HNO_3	*i*	—	1	—	—	—	—	2	—	—	—	—
La^{3+}–HNO_3	*i*	—	1	—	4	—	2	6	3	5	—	—
Ce^{4+}–HNO_3	*i*	—	2	—	—	—	—	1	—	—	—	3
Th^{4+}–HNO_3	*i*	—	2	—	1	—	3	6	4	5	7	8
UO_2^{2+}–HNO_3 ...	*j*	1	—	—	2	—	—	3	4	—	6	5
UO_2^{2+}–HNO_3 ...	*k*	1	—	—	2	—	—	3	—	4	—	5
R.E.–HNO_3	*l*	—	—	—	—	—	3	2	1	4	—	—

a, Present work. *b*, Knox and Spinks, *loc. cit.* *c*, Milner, Wood, and Woodhead, A.E.R.E. C/R 1041. *d*, Kutznetsov, *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 175. *e*, Axelrod and Swift, *J. Amer. Chem. Soc.*, 1940, **62**, 33; Nachtrieb and Fryxell, *ibid.*, 1948, **70**, 3552. *f*, McBryde and Yoe, *Analyt. Chem.*, 1948, **20**, 1094. *g*, West and Carlton, *Analyt. Chim. Acta*, 1952, **6**, 406. *h*, Wylie, *loc. cit.* *i*, Bock and Bock, *Z. anorg. Chem.*, 1950, **263**, 146. *j*, Warner, *loc. cit.* *k*, McKay *et al.*, *Trans. Faraday Soc.*, 1951, **47**, 428, 437; 1952, **48**, 997, 1099, 1103; 1954, **50**, 107.

Analytical Considerations.—The unfavourable volume changes which often occur on equilibration need not be a deterrent to the use of any particular solvent–acid system. Pre-treatment of either phase decreases the extent of volume changes at high initial acidities (Bock, Kusche, and Bock, *loc. cit.*), and miscibility may be decreased by the addition of salting out agents though these will certainly affect also the distribution ratios. An obvious device would be to alter the initial phase ratio from that employed in the present work.

Some of the solvents are not well suited to solvent-extraction procedures. Peroxidation was especially troublesome with 2 : 2′-dichlorodiethyl ether, but that of di*iso*propyl ether can be retarded by catechol. Methyl *iso*butyl ketone is the most convenient of the lower ketones since methyl *iso*propyl ketone formed emulsions readily with 0·02—0·05N-hydriodic acid and with hydrochloric acid of moderate strength. While these always broke in 10 min., emulsions formed by methyl *n*-propyl ketone sometimes persisted for 2—4 hr. *n*-Butaldehyde emulsified so readily that its examination was discontinued. Hydrolysis of esters increased with acidity and in the order hydriodic > hydrobromic > hydrochloric acid : it was noticeably rapid with ethyl acetate, but this appeared to present no great practical disadvantages. The inconvenient preparation of hydriodic acid free from iodine can be avoided by the effective device which produces the acid and a salting-out agent *in situ* from a mixture of sulphuric acid and potassium iodide (Irving and Rossotti, *Analyst*, 1952, **77**, 801).

Indium has been shown to be essentially quantitatively extracted from hydriodic acid or hydrobromic acid into a large variety of solvents. By use of a suitable solvent quantitative extraction into hydrochloric acid is also possible. However, for the purpose of separations from other metals, the use of the less efficient solvents is to be preferred. Removal of iron from indium by extraction of the former from hydrochloric acid into diethyl ether (Milner, *ibid.*, 1951, **76**, 488) or di*iso*propyl ether (Maxwell, Haymond, Bemberger, Garrison, and Hamilton, *J. Chem. Phys.*, 1949, **17**, 1006) has been claimed under conditions where the present results indicate that indium is also extracted. The ready extraction of indium into ketones, and probably the ready extraction of a number of other metallic halides which are known to be extracted only to a small extent into diethyl ether, is likely to find increasing applications in analysis.

Formation of Three-phase Systems.—Three phases in equilibrium resulted from *iso*propyl ether and solutions of indium in hydriodic acid at initial acidities greater than 4·95N. Three phases have also been reported in the system *iso*propyl ether–hydrochloric acid containing gallium (Nachtrieb and Fryxell, *J. Amer. Chem. Soc.*, 1949, **71**, 4035) and iron (Dodson, Forney, and Swift, *ibid.*, 1936, **58**, 2573), and with zinc or cobalt in the system thiocyanic acid–diethyl ether (Bock, *Z. anal. Chem.*, 1951, **133**, 110). In these systems the appearance of the third phase seems to be associated with a high concentration of metal, though this cannot be the explanation in the present instance. Similarly two phases are formed by relatively concentrated solutions of silver perchlorate in benzene and toluene (Hill, *J. Amer. Chem. Soc.*, 1922, **44**, 1163) and by NH_4AlCl_4, NH_4GaCl_4, or $LiGaCl_4$ in diethyl ether (Friedman and Taube, *ibid.*, 1950, **72**, 3362). It has been suggested that such behaviour is characteristic of highly polar substances in solvents of low dielectric constant (Friedman and Taube, *loc. cit.*), and a thermodynamic explanation has been advanced (Nachtrieb and Fryxell, *ibid.*, 1949, **71**, 4035). In the present system, as with others reported above, the denser organic phase is found to contain more metal than the lighter. Laurene (Ph.D. Thesis, Rensselaer Polytechnic Inst., 1952) has suggested that the extracted species is more highly hydrated in the denser phase. While our measurements demonstrate the presence of more water in the denser phase, it is not established that the additional water is bound to the acido-complex.

Volume Changes on Equilibration.—In consequence of a measure of mutual solubility the equilibration of equal volumes of organic and aqueous phase generally leads to striking volume changes which depend upon the particular solvent, and the nature and concentration of the halogen acid (cf. Experimental section). The volume of the aqueous phase generally increases at the expense of that of the organic phase, as shown for various ketones in Fig. 8, and for various ethers in Fig. 3 of Part I. For any one solvent these volume changes are more marked in the order hydriodic > hydrobromic > hydrochloric acid. For any given acid they become less pronounced on ascending a homologous series. Volume changes with 2 : 2′-dichlorodiethyl ether are negligible; with *iso*pentyl alcohol and acetate at high acidities the organic phase increases at the expense of the aqueous phase.

Equilibrium Acidities.—One result of an increase in the volume of an aqueous phase on equilibration is that the final concentration of acid, N, is less than the initial value, N'. The partition of acid itself into the organic phase at high concentrations contributes something to this decrease in N, and except in the case of 2 : 2′-dichlorodiethyl ether and *iso*pentyl alcohol and acetate, the final equilibrium acidities pass through a maximum value.

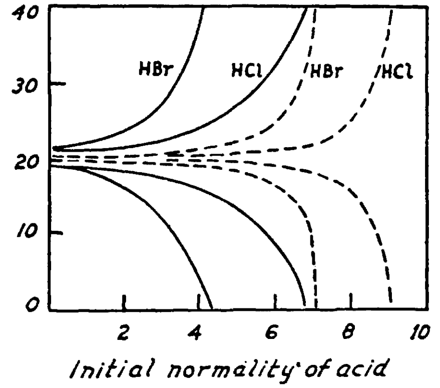
Values of this maximum acidity, N, and the corresponding initial acidities, N', are given in Table 4. They represent the maximum acidities attainable in the aqueous phase, starting with equal volumes of aqueous acid and organic solvent neither of which has been pre-saturated (" conditioned ") with the other phase. Increase in initial acidity beyond these critical values will merely result in a rapid approach to the point where the phases become completely miscible.

TABLE 4. *The maximum acidities, N, obtainable in equilibration of equal volumes of organic solvent and acid of initial normality N'.*

	HCl		HBr		HI	
Solvent	N	N'	N	N'	N	N'
Diethyl ether	4·8	7·0	3·5	5·0	2·0	3·0
Di*iso*propyl ether	7·3	8·0	5·6	6·0	4·2	5·0
Methyl propyl ketone	3·9	6·0	2·5	3·5	1·4	2·0
Methyl *iso*propyl ketone	3·8	6·0	2·4	3·0	2·1	2·5
Methyl *iso*butyl ketone	6·4	7·0	4·6	6·0	3·0	4·0
Ethyl acetate	4·5	5·8	3·1	4·0	1·7	2·4

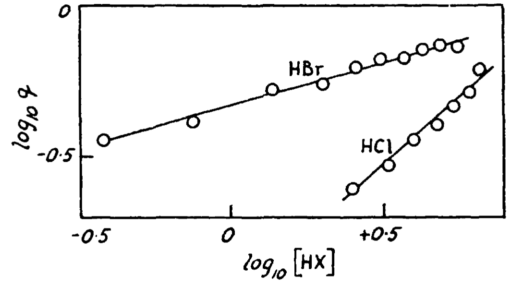
Water Content of the Organic Phases.—Determinations of the molar solubility of water in the organic phase after equilibration with hydrochloric and hydrobromic acid of various initial acidities are given for ethyl and *iso*pentyl acetate and pentyl alcohol, and diethyl and di*iso*propyl ether in the Experimental section. Determinations of the solubility of water in the absence of acids agree well with values in the literature (Durrans, " Solvents," Chapman and Hall, London, 1950). The solubility of water in *iso*pentyl alcohol increases markedly with acidity but in the remaining solvents it first decreases with increasing acidity but eventually rises again.

FIG. 8. *Volume changes on equilibration of 20 ml. of ketone and 20 ml. of halogen acid.*



—— *Methyl* iso*propyl ketone.*
– – – iso*Butyl methyl ketone.*

FIG. 9. *The extraction of halogen acids into* iso*pentyl alcohol.*



Extraction of Halogen Acids.—Partial miscibility with water appears to be a necessary, but not a sufficient, condition for the extraction of halogen acids into organic solvents. Thus the efficiency of *iso*pentyl alcohol as an extractant for acids is very much greater than that of the ethers which, in turn, are more effective than the hydrocarbons and their halogen derivatives. A recent process for the recovery of hydrochloric acid from industrial wastes utilises extraction with pentanols (Crittendon and Hixson, *Ind. Eng. Chem.*, 1954, **46**, 265).

Fig. 9 shows the dependence of the distribution ratio, q, on equilibrium acidity for the extraction of hydrogen chloride and bromide into *iso*pentyl alcohol. If undissociated hydrogen halide undergoes partition and exists as such in the organic phase (cf. Everett and Rasmussen, *J.*, 1954, 2812), then from equation (15) of Part I we can deduce that

$$\partial \log q/\partial \log C_{\mathrm{HX}} = \bar{\mathbf{h}} - \bar{h} \qquad (12)$$

where $\bar{\mathbf{h}}$ and $\bar{h}$ are the ligand numbers of hydrogen in the organic and aqueous phase respectively. The experimental value of this derivative is 0·88 for hydrochloric acid, implying 12% of association in the aqueous phase, provided $\bar{\mathbf{h}} = 1$. For hydrobromic acid the value of the gradient is only 0·29; but the association can scarcely be as high as 71% over the concentration range 0·5—9N. However, the derivation of equation (12) postulates that activity coefficients are constant throughout the range of acidities used, and that there are no changes of phase composition such as would invalidate the use of a constant stoicheiometric partition coefficient for the acids. Moreover there is evidence that hydrobromic acid is stronger than hydrochloric acid in aqueous solution (Ebert, *Naturwiss.*, 1925, **13**, 393; Robinson, *Trans. Faraday Soc.*, 1936, **32**, 743) and in glacial acetic acid (Bell and Skinner, *J.*, 1952, 2955; Kolthoff, *J. Amer. Chem. Soc.*, 1934, **56**, 1007). If this is true also in *iso*pentyl alcohol, *i.e.* if the acid is appreciably more dissociated in the organic phase, the lower value found for $\partial \log q / \partial \log C_{\mathrm{HBr}}$ would be explicable, for the ligand number $\bar{\mathbf{h}}$ in the organic phase would be less than unity (cf. Part I, equation 15).

For many other solvents investigated (but not reported here in detail) the partition of halogen acids at all moderate concentrations is so low that to a close approximation $NV = N'V'$. The amount of halogen acid extracted into diethyl and di*iso*propyl ether increases with increasing N', at first slowly and then rapidly above a critical concentration: even so the maximum value for the partition ratio is only $\sim 10^{-3}$ (Nachtrieb and Conway, *loc. cit.*; Bock, Kusche, and Bock, *loc. cit.*; Williams and Chalkley, Part II). While the addition of salts in macro-quantities is known to enhance the extraction of hydrochloric acid (Nachtrieb and Conway, *loc. cit.*; Garwin and Hixson, *Ind. Eng. Chem.*, 1949, **41**, 2298, 2303; Geankoplis and Garwin, *ibid.*, 1950, **42**, 1141) it can reasonably be assumed that the tracer quantities of indium used in the present experiments had comparatively little influence on the distribution of free acid and water in the system except in so far as water and halogen acid are involved in the formation of the extractable species and transported with it across the phase boundary. Variations in the distribution of acid and water can then be explained as follows.

According to Stokes and Robinson (*J. Amer. Chem. Soc.*, 1948, **70**, 1870) the hydration numbers of hydrochloric, hydrobromic, and hydriodic acid are 8·0, 8·6, and 10·6 respectively. Hence at concentrations of approximately 6, 5·5, and 4·4N respectively, all the water in such solutions will be effectively bound to the halogen acid. The withdrawal of water from the organic phase to solvate halogen acid should thus increase with concentration, as observed, up to certain critical values. At still higher concentrations the dissolved halogen acids could not be fully hydrated and the solvation sheaths would be completed by organic molecules (provided these have a sufficiently marked donor character) withdrawn from the organic phase. In view of the organic content of the aqueous phase the critical maximum acidities will differ from those estimated above for the pure acids and will depend on the nature of the organic solvent and the extent to which it can co-ordinate competitively with water to the particular halogen acid. Such factors are apparent in Table 4, for the maximum acidities, although invariably decreasing in the order HCl > HBr > HI, are not the same for any one acid. As increasing amounts of organic solvent dissolve in the aqueous phase its dielectric constant will fall. This will favour the association of hydrogen and halide ions and will thus increase the extraction of undissociated acid into the almost anhydrous organic phase. If the halogen acid is extracted as a hydrated ion-pair, much as is indium bromide which is shown to be extractable as the hydrated acido-complex $\mathrm{HInBr_4,10H_2O}$ (Part III and IV), the amount of water in the organic phase will increase again.

Such explanations cannot be applied to the systems involving *iso*pentyl alcohol. Here volume changes are in the opposite sense to those previously discussed and large amounts of water and halogen acid pass into the organic phase as the initial acidity is increased. It appears that the solubility of water in *iso*pentyl alcohol is so high (in consequence of hydrogen bonding) that hydrated halogen acids are able to undergo partition freely, so that the distribution of both water and acid increases with increasing acidity. It has also been suggested that the presence of halogen acid lowers the difference in internal pressures between aqueous and organic phases and so promotes miscibility (Crittendon and Hixson, *loc. cit.*; Reburn and Shearer, *J. Amer. Chem. Soc.*, **1933**, **55**, 1774). The behaviour of *iso*pentyl acetate at high acidities is doubtless due to the production of *iso*pentyl alcohol by hydrolysis. Hydrolysis was also apparent in measurements with ethyl acetate, and since its extent will be a function of the duration of equilibration as well as of acidity the figures given for volume changes and water content have no absolute significance, though they indicate how the system behaves in certain circumstances.

The general treatment of solvent extraction outlined in Part I is only strictly applicable to " ideal systems " but its use in discussing the frequently highly " non-ideal " systems encountered in the solvent extraction of indium halides described in the present paper has at least permitted a semiquantitative interpretation of the results in most cases. While the results are of immediate analytical interest, it is clear that a complete understanding of the physical chemistry of an individual system can be achieved only through a detailed investigation from a more fundamental standpoint such as that adopted in the investigation of the physical chemistry of uranyl nitrate solutions (cf. McKay, *Chem. and Ind.*, 1954, 1549, and refs. therein).

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