similar conditions are stable for many hours.

The absorption curves of the metallochlorin "bleached" products are qualitatively similar to the curves for irreversible "bleaching" of chlorophyll by oxygen in acetone, as reported by Aronoff and MacKinney.[5] Furthermore, in the same paper, these authors report a value of 5×10^{-4} for the quantum yield of irreversible "bleaching" of chlorophyll solutions in benzene. This is in order of magnitude agreement with our value of 9.4×10^{-4} for the quantum yield of the photo-oxidation of magnesium chlorin by oxygen.

(5) Aronoff and MacKinney, THIS JOURNAL, **65**, 956 (1943).

Summary

1. Zinc and magnesium tetraphenylchlorins may be photo-oxidized by molecular oxygen in a manner similar to ortho- and para-quinones.

2. Oxygen does not inhibit a chlorin–quinone reaction but merely reacts competitively with the quinone for the chlorin (at least for quinones of lower oxidation potential than oxygen).

3. A secondary reaction occurs between hydrogen peroxide and the porphin yielding a product similar to that obtained by "bleaching" chlorophyll in the presence of oxygen.

BERKELEY, CALIFORNIA RECEIVED APRIL 12, 1949

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, THE UNIVERSITY OF CHICAGO]

The Extraction of Gallium Chloride by Isopropyl Ether

BY NORMAN H. NACHTRIEB AND ROBERT E. FRYXELL

The distribution of gallium chloride between aqueous hydrochloric acid and diethyl ether has received the attention of several workers. Grahame and Seaborg[1] report that the distribution is independent of gallium concentration in the range 10^{-12} to 10^{-3} molar, but Swift[2] reports a relatively greater extraction for higher concentrations.

It is well known that the distribution of gold chloride[3,4] and ferric chloride[5,6,7,8] between aqueous hydrochloric acid and ethers is dependent on the concentration of the metal chloride. In a recent paper the present authors reported data for ferric chloride showing that this distribution (using isopropyl ether) follows the simple Nernst distribution law for sufficiently low ferric chloride concentrations.[7] It was suggested that the existence of polymers in the ether phase need not be postulated to explain the dependence of the distribution on iron at higher concentrations, but alternatively, the anomaly may be due to a self-promoted activity of ferric chloride in the aqueous phase.

This paper reports a similar study which has been made of the distribution of gallium chloride between aqueous hydrochloric acid and isopropyl ether.

Experimental

Preparation of Solutions.—For the majority of the experiments, radioactive Ga^{72} was used to facilitate analysis. The gallium was received as a mixture of oxide and nitrate.[9] A solution was prepared by dissolving 0.0559 g. of this material in 20.0 ml. of 7.30 molar hydrochloric acid, purified by extraction with two 20-ml. portions of isopropyl ether, and won back from the ether with water to provide a gallium tracer solution. This solution was diluted to 50.0 ml. It was assigned a concentration of 0.00594 M, based upon a gravimetric determination of the gallium in the oxide–nitrate mixture after its activity had decayed.

A stock solution of inactive gallium chloride was prepared as follows: 5.1457 g. of gallium metal (99.9%) was dissolved in hot aqua regia, evaporated to a sirupy consistency twice with 10-ml. portions of concentrated nitric acid, and finally taken to dryness. The residue was heated at *ca.* 260° until the nitrate was completely converted to oxide. An excess of concentrated hydrochloric acid (20.0 ml.) was added; warming effected complete solution. It was discovered that by warming and blowing air over the surface of this solution, a gel formed which would not redissolve on dilution. Apparently, this was a basic salt, since addition of a few ml. of hydrochloric acid caused solution. Aeration of the solution at room temperature was successful in removing the small excess of hydrochloric acid. Analysis of this solution after dilution to 75.0 ml. gave: $(Ga) = 0.8957\ M$, $(Cl^-) = 2.677\ M$.

The isopropyl ether was purified by shaking with alkaline potassium permanganate solution, drying over calcium chloride, and distilling. The fraction boiling in the range 66.5 to 67.5° at 747.1 mm. was collected.

Analytical Methods.—Measurement of the radioactivity of the samples served as a determination of relative concentrations of gallium. Aliquots of solutions were evaporated just to the point of dryness under an infrared lamp on 1" copper disks having spun-up edges. Counting rates were determined with a thin-wall mica window Geiger–Müller tube in conjunction with a Higginbotham type scaler. Whenever possible, a total count of at least 5,000 was registered. The background of the counter was 28 counts/minute. The statistical error was probably lower than the errors due to self-absorption and to handling an isotope with a half life of only fourteen and one-tenth hours. The latter error was minimized by counting consecutively the copper disks corresponding to the ether and aqueous phases of a single extraction.

Gallium analyses listed in Table I and those noted in Table II were performed by the 8-hydroxyquinoline–potassium bromate titration method as described by Kolt-

(1) D. C. Grahame and G. T. Seaborg, THIS JOURNAL, **60**, 2524 (1938).

(2) E. H. Swift, *ibid.*, **46**, 2375 (1924).

(3) W. A. E. McBryde and J. H. Yoe, *Anal. Chem.*, **20**, 1094 (1948).

(4) F. Mylius and C. Hüttner, *Ber.*, **44**, 1315 (1911).

(5) R. W. Dodson, G. J. Forney and E. H. Swift, THIS JOURNAL, **58**, 2573 (1936).

(6) J. Axelrod and E. H. Swift, *ibid.*, **62**, 33 (1940).

(7) N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **70**, 3552 (1948).

(8) C. H. Craft and G. R. Makepeace, *Ind. Eng. Chem., Anal. Ed.*, **17**, 206 (1945).

(9) Supplied by Isotopes Branch, United States Atomic Energy Commission, Oak Ridge, Tennessee.

hoff and Sandell.[10] This method was checked against the hydroxide precipitation method[11] and found to be good to 0.5% with 5–15 mg. of gallium. The method was also used to demonstrate that significant amounts of gallium were not lost in the evaporation of solutions on the copper counting disks.

Free acid was calculated from titrations with standard sodium hydroxide, allowing for the quantity of base consumed in the precipitation of gallium hydroxide. Brom cresol purple was the indicator used. The validity of this calculation is discussed later.

Determinations of chloride were made by the Fajans method on the solution remaining from the acidity determination. Dichlorofluorescein was the indicator used.

Extraction Procedure.—In an experiment similar to the one reported by Nachtrieb and Conway for ferric chloride,[12] extraction equilibrium was found to be established within six minutes. All extractions were carried out in 10-ml. glass-stoppered cylinders with 5.0 ml. of isopropyl ether and 5.0 ml. of aqueous solution of known gallium chloride and hydrochloric acid concentrations, except as noted. Cylinders were alternately thermostatted at 20.0 ± 0.1° and mixed by inversion for a total time of at least thirty minutes. The two phases were separated with pipets and transferred to stoppered test-tubes. Before the aliquots were taken for analysis, the tubes were centrifuged for several minutes to separate any small amount of the other phase.

The equilibrium concentrations of gallium in the aqueous and ether phases were calculated by solving sets of simultaneous equations of the type

$$a(\mathrm{Ga})_{\mathrm{aq}} + b(\mathrm{Ga})_{\mathrm{eth}} = c(\mathrm{Ga})_{\mathrm{initial}} \qquad (1)$$

$$\frac{(\mathrm{Ga})_{\mathrm{eth}}}{(\mathrm{Ga})_{\mathrm{aq}}} = \frac{\text{ether counting rate (counts/ml./min.)}}{\text{aqueous counting rate (counts/ml./min.)}} \qquad (2)$$

where c is the initial aqueous volume and a and b are the final volumes of the aqueous and ether phases, respectively.

Discussion of Results

Empirical Formula of the Gallium Complex in the Ether Phase.—Analyses of a number of ether phases for gallium, chloride and ionizable hydrogen gave the results shown in Table I. The values given for hydrogen and chloride have been corrected for the solubility of hydrochloric acid in isopropyl ether as given by Nachtrieb and Conway.[12] The empirical formulas tabulated in the last column show that essentially equimolecular amounts of hydrochloric acid and gallium chloride are co-extracted from aqueous solutions initially less than 7 M hydrochloric acid. The fourth formula listed is far different from $HGaCl_4$. It may be that the solubility of hydrochloric acid in isopropyl ether is altered by the presence of the gallium complex and that the correction applied is too large. If so, the error is relatively larger for this particular sample, in which the total concentrations were quite low.

Extractions from 8 M hydrochloric acid gave $HCl:GaCl_3$ ratios significantly greater than unity. These formulas may correspond to conditions favoring the formation of complex molecules containing more than one HCl. Nevertheless, it seems clear that the empirical formula for the gallium complex is quite analogous to that determined for iron.[12]

All gallium analyses reported in Table I were made by the 8-hydroxyquinoline–potassium bromate method. It is interesting to note that the total cation concentration (hydrogen plus gallium) is usually 2–3% lower than the chloride concentration. This may represent an error in the calculation used in determining free acid, in which the assumption is made that gallium has consumed exactly three hydroxide ions at the brom cresol purple end-point. Potentiometric titrations were performed using a calomel–glass electrode system, but although the indicator end-point appeared slightly before the inflection in the potentiometric curve, the discrepancy was much less than the 2–3% error in the charge balance. The disagreement may be due to the occlusion of gallium salts within the gelatinous hydroxide or the precipitation of a basic gallium salt requiring less than three equivalents of hydroxide. A similar observation has been noted by Fricke and Meyring.[13]

TABLE I

ANALYSES OF ETHEREAL PHASES

$[HCl]_i$	$[Ga]_{eth}$	$[Cl]_{eth}$ (cor.)[a]	$[H]_{eth}$ (cor.)[a]	Empirical formula
3.00	0.0823	0.3342	0.0898	$H_{1.09}GaCl_{4.06}$
4.00	.4126	1.614	.3480	$H_{0.84}GaCl_{3.91}$
4.00	.0551	0.2162	.0475	$H_{0.86}GaCl_{3.93}$
4.00	.00402	.0127	.00141	$H_{0.35}GaCl_{3.17}$
5.00	1.210	5.114	1.354	$H_{1.12}GaCl_{4.23}$
5.00	0.4448	1.825	0.453	$H_{1.02}GaCl_{4.10}$
6.00	.5294	2.139	.5024	$H_{0.95}GaCl_{4.04}$
6.00	.1566	0.6348	.1529	$H_{0.98}GaCl_{4.05}$
6.00	.0532	.2151	.0505	$H_{0.95}GaCl_{4.04}$
7.00	1.484	6.140	1.553	$H_{1.05}GaCl_{4.14}$
7.00	1.097	4.847	1.423	$H_{1.31}GaCl_{4.42}$
7.00	0.3829	1.672	0.496	$H_{1.30}GaCl_{4.37}$
7.00	.3446	1.462	.420	$H_{1.22}GaCl_{4.24}$
8.00	1.080	4.782	1.430	$H_{1.33}GaCl_{4.43}$
8.00	1.298	5.529	1.530	$H_{1.18}GaCl_{4.25}$
8.00	0.3076	1.469	0.562	$H_{1.82}GaCl_{4.77}$
8.00	.4081	1.960	.689	$H_{1.69}GaCl_{4.80}$ (heavy ether)
8.00	.0397	0.2086	.0788 [b]	$H_{1.98}GaCl_{5.25}$ (light ether)
8.00	.4796	2.213	.740	$H_{1.54}GaCl_{4.61}$ (heavy ether)
8.00	.1391	0.576	.196 [b]	$H_{1.41}GaCl_{4.14}$ (light ether)
8.00	1.137	4.801	1.262	$H_{1.11}GaCl_{4.22}$ (heavy ether)[c]
8.00	0.546	2.298	0.673	$H_{1.23}GaCl_{4.21}$ (heavy ether)[c]
9.00	.580	2.543	.732	$H_{1.26}GaCl_{4.38}$

[a] Corrected for the solubility of hydrochloric acid in isopropyl ether. [b] Heavy and light phases from a single extraction. [c] The corresponding light phases not analyzed.

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., revised edition, 1943, p. 638. Credit is due Dr. L. P. Pepkowitz for demonstrating that the method is applicable to gallium.

(11) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 388.

(12) N. H. Nachtrieb and J. G. Conway, THIS JOURNAL, **70**, 3547 (1948).

(13) R. Fricke and K. Meyring, *Z. anorg. Chem.*, **176**, 325 (1928.)

Variation of the Distribution Coefficient with Gallium Chloride Concentration.—Similar to the case of ferric chloride,[7] it can be shown that on the assumption of a polymerized gallium complex in the ether phase, the distribution expression would be

$$(Ga)_{n\ eth}/(Ga)^{n}_{aq} = K_{(H^+),(Cl^-)\ constant} \quad (3)$$

under conditions of constant aqueous hydrogen and chloride ion activities. The stoichiometric gallium concentration as analytically determined will be proportional to the concentration of the ion species which takes part in the distribution equilibrium under these conditions. Equation (3) may be expressed in the form

$$\log (Ga)_{n\ eth} = \log K + n \log (Ga)_{aq} \quad (4)$$

from which it appears that the association number n would be the slope of a plot of the logarithm of the ethereal gallium activity against the logarithm of the aqueous gallium activity for extractions performed under conditions of constant aqueous hydrogen and chloride activity and of varying total gallium concentration.

Table II gives the initial gallium chloride and hydrochloric acid concentrations, the initial and final phase volumes, the final gallium concentrations and the distribution ratios at various initial hydrochloric acid concentrations. Figure 1 is a plot of the data in Table II. These curves are similar to those obtained for ferric chloride.[7] At sufficiently low gallium concentrations the slope is unity, corresponding to the "ideal" behavior predicted by the simple Nernst distribution equation. With increasing gallium concentration the slope increases sharply, and for higher acidities passes through a maximum, then decreases, becoming less than unity. The decrease in slope at these high gallium concentrations may be due to several causes, such as (1) decrease in the aqueous hydrochloric acid concentration due to its extraction, and (2) the approach to saturation of the gallium complex in the ether phase (see below).

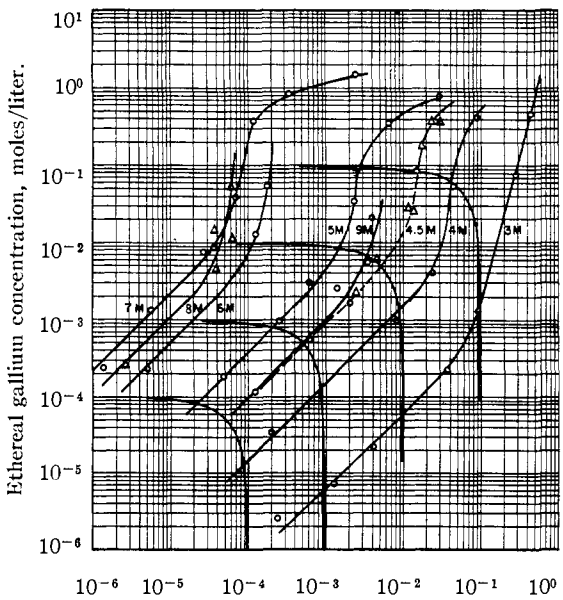

Fig. 1.—Variation of distribution with gallium concentration for several hydrochloric acid concentrations.

Variation of the Distribution Coefficient with Aqueous Hydrochloric Acid Concentration.—In Fig. 2 are plotted the distribution coefficients as a function of acidity for several initial gallium concentrations. These are taken from the intersections of the distribution curves with the rectangular hyperbolas (representing initial gallium concentrations) drawn in Fig. 1. The optimum acidity for efficient extraction is about 7.2 molar. It is evident that up to 0.01 molar, the distribution is essentially independent of gallium concentration, especially for the lower acidities. The salting-out effect, as postulated for the case of ferric chloride,[7] (if this be the cause of the changing slope in Fig. 1) becomes important above 0.01 molar gallium concentrations.

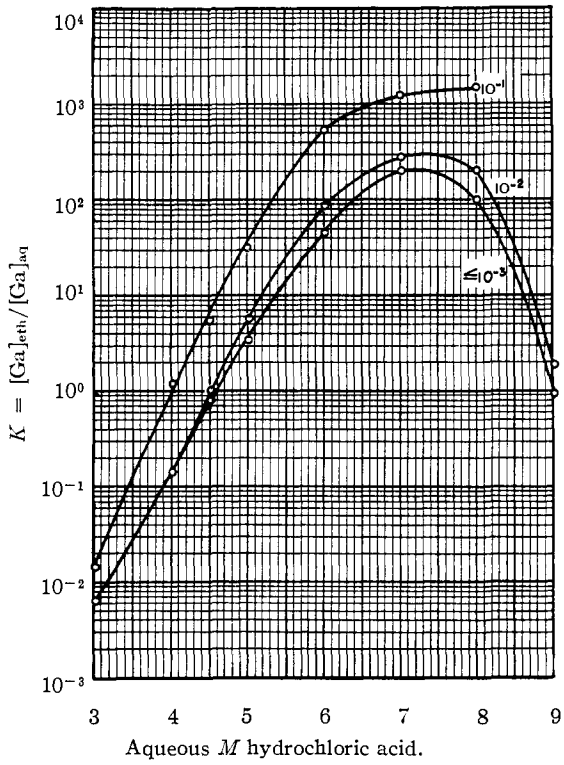

Fig. 2.—Variation of distribution coefficient with hydrochloric acid concentration for several initial gallium chloride concentrations.

Appearance of a Three Phase System.—For extractions made from 8.00 and 9.00 M hydrochloric acid, increase in the concentration of gallium chloride caused the separation of a

TABLE II

DISTRIBUTION OF GALLIUM CHLORIDE BETWEEN AQUEOUS HYDROCHLORIC ACID AND ISOPROPYL ETHER

$[HCl]_i$ [a]	$[Ga]_i$	$[Ga]_{aq}$	$[Ga]_{eth}$	Volume, ml. Aqi	Ethi	Aqfinal	Ethfinal	$K = [Ga]_{eth}/[Ga]_{aq}$
3.00	0.8981	0.4360	0.4774	5.00	5.00	4.60	5.21	1.095
3.00	.3597	.2864	.0760	5.00	5.00	4.98	4.92	0.265
3.00	.0920	.0896	.00126	5.00	5.00	5.06	4.88	.0141
3.00	.0373	.0355	.000218	5.00	5.00	5.21	4.92	.00613
3.00	.00924	.00907	5.75×10^{-5}	5.00	5.00	5.06	4.93	.00634
3.00	.00408	.00397	2.18×10^{-5}	5.00	5.00	5.10	4.85	.00548
3.00	.00119	.00116	7.12×10^{-6}	5.00	5.00	5.10	4.88	.00615
3.00	.000238	.000231	2.53×10^{-6}	5.00	5.00	5.08	4.92	.0109
4.00[b]	.5156	.0895	0.4126	5.00	5.00	4.68	5.12	4.61
4.00[b]	.1031	.0454	.0551	5.00	5.00	5.00	4.90	1.21
4.00[b]	.0309	.0243	.00402	50.00	50.00	50.5	49.5	0.165
4.00	.000238	2.01×10^{-4}	3.35×10^{-5}	5.00	5.00	5.10	4.90	.167
4.00[b]	.00937	0.00816	0.00101	100	100	101	99	.124
4.50	.4031	.0307	.3536	5.00	5.00	4.71		11.5
4.50	.4028	.0234	.3794	5.07	5.00			16.2
4.50	.2019	.0181	.1859	5.00	5.00	4.90		10.3
4.50	.1013	.0155	.0858	5.00	5.00	5.00		5.55
4.50	.0409	.0119	.0291	5.00	5.00	5.03		2.45
4.50	.0409	.0141	.0268	5.00	5.00			1.90
4.50	.0107	.00472	.00605	5.00	5.00	5.09		1.28
4.50	.00471	.00249	.00221	5.00	5.00	5.10		0.89
5.00	.8962	.0307	.7750	5.00	5.00	4.30	5.40	26.2
5.00	.3588	.00676	.3483	5.00	5.00	4.83	5.06	51.5
5.00	.0901	.00280	.0892	5.00	5.00	5.05	4.89	31.9
5.00	.0363	.00240	.0352	5.00	5.00	5.10	4.80	14.7
5.00	.00829	.00140	.00704	5.00	5.00	5.11	4.87	5.03
5.00	.00360	.000652	.00303	5.00	5.00	5.13	4.83	4.65
5.00	.00119	.000266	.000945	5.00	5.00	5.11	4.85	3.55
5.00	.000238	.0000506	.000191	5.00	5.00	5.16	4.83	3.78
6.00[b]	.05156	.000180	.0532	100.0	100.0	102	96	296
6.00[b]	.00111	.000126	.0125	225.0	25.0	231.6	16.8	99.5
6.00	.000238	4.96×10^{-6}	2.44×10^{-4}	5.00	5.00	5.18	4.77	49.1
7.00	1.3441	0.00262	1.460	5.00	5.00	3.95	5.60	556
7.00	0.8962	.000346	0.860	5.00	5.00	4.39	5.21	2490
7.00[b]	.3918	.000120	.383	12.5	12.5	12.3	12.3	3191
7.00	.3227	.000555	.336	5.00	5.00	5.00	4.80	605
7.00[b]	.2062	.000341	.825	40.0	10.0	39.7	9.5	2420
7.00	.0901	.000100	.0955	5.00	5.00	5.16	4.71	952
7.00	.0363	.0000700	.0394	5.00	5.00	5.25	4.63	560
7.00	.00829	3.67×10^{-5}	.00887	5.00	5.00	5.25	4.65	242
7.00	.00119	5.79×10^{-6}	.00128	5.00	5.00	5.26	4.63	221
7.00[b]	.000462	2.73×10^{-5}	.00763	450	50.0	471	29	279
7.00	.000238	1.36×10^{-6}	.000254	5.00	5.00	5.25	4.65	187

[a] i signifies initial concentrations and volumes. [b] Gallium analysis by 8-hydroxyquinoline method.

third liquid phase intermediate in density between the aqueous and ether phases, formed at the expense of the ether phase.[14] Near the lower gallium concentration limit of the three-phase region the volume of the intermediate ("heavy ether") phase is comparatively small, becomes larger at higher concentrations of gallium chloride, and at extremely high concentrations, the system again becomes two phase. Data obtained at 8.00 and 9.00 *M* hydrochloric acid are collected in Table III. The distribution coefficients at gallium concentrations below the three phase region are also plotted in Fig. 1. It is felt that the appearance of the third phase is related to the solubility of the gallium complex in isopropyl ether and, thus, the ether layer in the two phase system at very high gallium concentrations is considered "heavy." It is interesting to note that the ratio $(Ga)_{heavy\ ether}/(Ga)_{light\ ether}$ is relatively more constant than the other two possible distribution coefficients. This is reflected in the columns $(Ga)_{light\ ether}$ and $(Ga)_{heavy\ ether}$. However, with such a limited number of data, no conclusions can be drawn concerning the nature

(14) In the analogous system, ammonium chlorogallate in anhydrous diethyl ether, a second ether phase has been observed at high ammonium chlorogallate concentrations (H. Friedman, Dissertation, The University of Chicago, 1949).

TABLE III

DISTRIBUTION OF GALLIUM CHLORIDE BETWEEN AQUEOUS HYDROCHLORIC ACID AND ISOPROPYL ETHER

					Volume, ml.					K =		
$[HCl]_i$	$[Ga]_i$	$[Ga]_{aq}$	$[Ga]_{l.eth.}$	$[Ga]_{heavy}$	Aqi	Ethi	Aqfinal	Ethfinal	Heavy ether	$\frac{[Ga]_{l.eth}}{[Ga]_{aq}}$	$\frac{[Ga]_{h.eth}}{[Ga]_{aq}}$	$\frac{[Ga]_{h.eth}}{[Ga]_{l.eth}}$
8.00	0.8962	0.000575		0.855	5.00	5.00	4.44	5.24			1487	
8.00	.9040	.00432		.860	5.00	5.00	4.42	5.23			199	
8.00	.9185	.00656		.874	5.00	5.00	4.40	5.22			133	
8.00	.2886	.000111		.318	5.00	5.00	5.26	4.55			2866	
8.00	.1882	.000879	0.0469	.419	5.00	5.00	5.40	2.43	1.97	53.4	476	8.93
8.00	.2021	.000672	.0699	.374	5.00	5.00	5.32	2.21	2.28	104	556	5.35
8.00	.0905	.0000983	.0585	.331	5.00	5.00	5.57	3.70	0.71	595	3370	5.66
8.00	.0954	.000316	.0619	.354	5.00	5.00	5.60	3.68	.70	196	1120	5.71
8.00	.0368	.000163	.0445		5.00	5.00	5.60	4.12	.10	272		
8.00	.00876	.0000604	.0103		5.00	5.00	5.69	4.23		170		
8.00	.00408	.0000385	.00469		5.00	5.00	5.60	4.30		122		
8.00[a]	.00111	5.88×10^{-5}	.0559		225	25.0	244	6.0		951		
8.00	.000238	2.72×10^{-6}	.000272		5.00	5.00	5.62	4.30		100		
8.00[a]	.000231	3.55×10^{-5}	.0148		450	50.0	490	6		417		
9.00	.6275	0.00187		.666	5.00	5.00	5.02	4.69			356	
9.00	.9175	.00255		.879	5.00	5.00	4.37	5.21			344	
9.00	.2062	.00204	.0302	.459	5.00	5.00	6.16	1.50	2.12	14.85	226	15.2
9.00	.2305	.0143	.0450	.421	5.00	5.00	6.27	0.91	2.43	3.14	29.4	9.4
9.00	.0901	.00297	.0227	.534	5.00	5.00	6.50	2.52	0.70	7.62	180	23.5
9.00	.0905	.0109	.0256	.498	5.00	5.00	6.79	2.35	.64	2.34	45.5	19.4
9.00	.0368	.00397	.0210	.561	5.00	5.00	6.70	2.96	.17	5.28	141	26.8
9.00	.00829	.00364	.00553		5.00	5.00	6.75	3.05		1.52		
9.00	.00360	.00140	.00268		5.00	5.00	6.57	3.28		1.91		
9.00	.00384	.00210	.00167		5.00	5.00	6.70	3.09		0.80		
9.00	.00119	.000635	.000548		5.00	5.00	6.80	2.96		0.86		
9.00	.000238	.000124	.000115		5.00	5.00	6.75	3.05		0.93		

[a] Gallium analysis by 8-hydroxyquinoline method.

and origin of the three phase system. For this purpose further investigation will be necessary. Measurement of densities, refractive indices and molecular weights would be highly desirable.

The dependence of the distribution coefficient on gallium concentration, the empirical formula of the gallium complex in the ether phase and the appearance of the third phase at high acid and gallium concentrations demonstrate a strong similarity of the gallium chloride and ferric chloride systems. (The third phase in the iron system has been reported by Dodson and co-workers[5].) It is unfortunate that the gallium solutions are not amenable to absorption spectrum measurements in the visual region. For $HFeCl_4$ in isopropyl ether, Beer's law conformity was observed for iron concentrations ranging from 0.01 to 0.4 molar.[12] By analogy, this lends support to the hypothesis that the anomalous distribution of gallium chloride between aqueous hydrochloric acid and isopropyl ether may be due to a salting-out effect and not necessarily to a polymerization of the gallium complex in the ether phase.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Miss M. C. Bachelder who performed many of the gravimetric analyses, and of Mr. Lyle Raub, who helped in conducting the experiments with the radioactive isotope. The authors are also indebted to Dr. William L. Fink of the Aluminum Company of America for making available some of the gallium used in the investigation.

Summary

The distribution of gallium chloride between aqueous hydrochloric acid and isopropyl ether has been found to obey the simple Nernst partition law for low gallium concentrations. At concentrations of gallium exceeding 0.01 molar, the partition increases in favor of the ether phase. The empirical formula of the gallium complex in the ether phase is $HGaCl_4$, if extracted from an aqueous solution not exceeding 7 molar hydrochloric acid.

Under certain conditions, a third ether-rich phase has been observed.

CHICAGO 37, ILLINOIS RECEIVED MAY 23, 1949