342. *Studies in the Chemistry of Quadrivalent Germanium. Part IV.* The Chemical Nature of Solutions of Quadrivalent Germanium in Hydrochloric or Hydrobromic Acid.*

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Solubility measurements and anion-exchange studies have indicated that anionic germanium chloro-complexes of the type $[Ge(OH)_xCl_{5-x}]^-$ or $[Ge(OH)_xCl_{5-x}]^{2-}$, where x lies between 3 and 4, are the principle germanium species present in 6—9M-hydrochloric acid solutions. Below 6M-hydrochloric acid, these complexes are hydrolysed to germanium dioxide, and above 9M-hydrochloric acid they are converted into germanium tetrachloride. No evidence has been found for the existence of any germanium bromo-complexes in hydrobromic acid solution.

LITTLE information exists as to the chemical nature of solutions of germanium tetrachloride in hydrochloric acid of sufficient strength to prevent hydrolysis to germanium dioxide (*i.e.*, >6M). Allison and Muller [1] showed that the solubility of germanium tetrachloride increased from a low value in 12M-hydrochloric acid to a maximum value in 7·8M-acid. Pugh [2] showed that the solubility of germanium dioxide was a minimum in 6N-hydrochloric acid, but that its solubility increased at higher acid concentrations. No quantitative experiments were made by these authors at acid concentrations between 6 and 7·8M. Transport experiments [3] failed to establish the presence of anionic germanium complexes in hydrochloric acid solutions, although it was possible to isolate cæsium hexachlorogermanate under the correct conditions.

Adsorption of germanium on a large excess of anion-exchange resin from very dilute solutions of quadrivalent germanium in hydrochloric acid has been reported by Yoshino [4] and by Nelson and Kraus.[5] This work gave little information, however, concerning the complexes which occur in more concentrated germanium solutions. In the present work, ion-exchange experiments have been carried out with solutions of quadrivalent germanium in hydrochloric acid, under conditions which allowed sufficient germanium to be sorbed by the resin to enable the formulæ of the sorbed germanium complexes to be calculated by the usual methods (cf., *e.g.*, Salmon [6]).

EXPERIMENTAL

Solubility Measurements.—The solubilities of germanium dioxide tetrachloride and bromide in hydrochloric and hydrobromic acid were determined by shaking excess of the germanium compound with the required acid at room temperature for 2—3 weeks, and then analysing the solution phase for germanium. The solutions obtained in this way were used in the equilibrium experiments with the anion-exchangers.

Anion-exchangers.—Analytical Grade Amberlite I.R.A. 400, in the chloride or bromide form, was used throughout; 0·25 g. of the air-dried chloride form of the batch of resin used had a capacity of *ca.* 0·73 milliequiv.

Analytical Methods.—Germanium was determined iodometrically after reduction to the bivalent state.[7] Halogens were determined gravimetrically as the silver halide. Rubidium was determined by first volatilising germanium by fuming with 12M-hydrochloric acid, fuming with sulphuric acid, and igniting to rubidium sulphate.

Anion-exchange Experiments.—Continuous shaking for 24 hr. was allowed for establishment

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* Part III, *J.*, 1955, 4415.

[1] Allison and Muller, *J. Amer. Chem. Soc.*, 1932, **54**, 2833.

[2] Pugh, *J.*, 1929, 1537.

[3] Laubengayer, Billings, and Newkirk, *J. Amer. Chem. Soc.*, 1940, **62**, 546.

[4] Yoshino, *Bull. Chem. Soc. Japan*, 1955, **28**, 382.

[5] Nelson and Kraus, *J. Amer. Chem. Soc.*, 1955, **77**, 2133.

[6] Salmon, *Rev. Pure Appl. Chem.* (*Australia*), 1956, **6**, 24.

[7] Everest, *J.*, 1953, 4117.

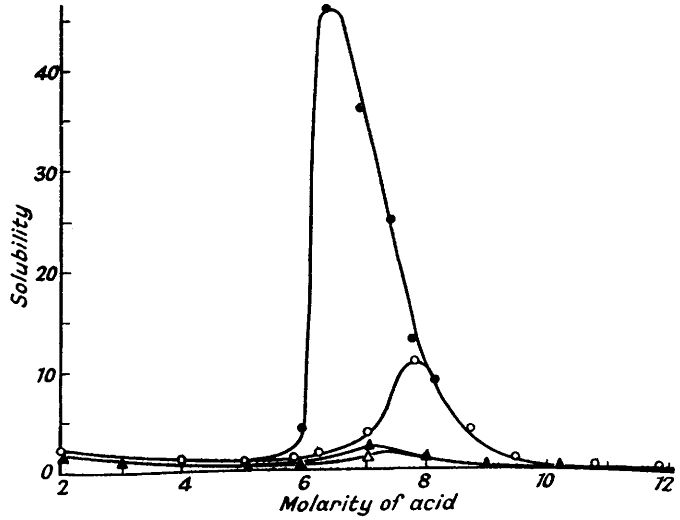
of equilibrium between the resin and the solution phase, experiments for longer periods showing this to be sufficient. The bulk of the solution was then decanted from the resin, and the latter transferred to a column (1 cm. int. diam., 10 cm. long above the sintered disc of No. 2 grade porosity) with the minimum amount of hydrochloric acid of the same normality as in the original solution. The acid adhering to the outside of the resin particles was removed by flushing the column for 2—3 sec. with water under high suction. The resin was then eluted with 0·1M-sodium hydroxide (250 ml.) for 24 hr. to remove germanium and chloride, which were then determined in the eluate. Blank experiments with 6—8M-hydrochloric acid and 0·25 g. of resin showed that a value of 0·05 milliequiv. had to be subtracted from the value of the chloride sorbed by the resin in order to correct for the free acid present in the resin phase.

Rubidium Hexachlorogermanate.—To a saturated solution of germanium tetrachloride in 7M-hydrochloric acid (15 ml.) was added a solution of rubidium chloride (1·5 g.) in 7M-hydrochloric acid (5 ml.); on cooling, crystals of the *salt* separated (Found: Rb, 37·0; Ge, 15·6; Cl, 46·8. Rb_2GeCl_6 requires Rb, 37·4; Ge, 15·9; Cl, 46·6%). Cæsium hexachlorogermanate was prepared by an analogous reaction.

RESULTS

Solubility Measurements.—The solubilities of germanium dioxide and tetrachloride in hydrochloric acid are shown in the Figure. The salient feature is the large divergence between the solubility curves for germanium dioxide and tetrachloride at hydrochloric acid concentrations between 6 and 8M, indicating that the simple equilibrium $GeO_2 + 4HCl \rightleftharpoons GeCl_4 + 2H_2O$ does not hold in this acid concentration range. The corresponding divergence, and the actual germanium solubilities, are much smaller in the hydrobromic acid solutions. All solutions of germanium tetrachloride in hydrochloric acid are stable above 7M-hydrochloric acid with respect to hydrolysis, no precipitate of germanium dioxide occurring even after one year. Similar solutions in 6M-hydrochloric acid, or below, begin to afford precipitates of germanium dioxide after a few hours and may continue to do this for several weeks. Solutions in 6·5M-hydrochloric acid are stable for some 4—5 months but then begin to slowly deposit germanium dioxide. The solubility of germanium tetrachloride in 6—8M-hydrochloric acid showed an inverse temperature coefficient of solubility; solubilities found were: 49·3 g./l. of germanium dioxide at −15°, 46·3 at 0°, 38·7 at 15°, and 33·5 at 35°.

Solubilities of germanium tetrachloride and germanium dioxide in hydrochloric acid and of germanium tetrabromide and germanium dioxide in hydrobromic acid.



● Germanium tetrachloride in hydrochloric acid.
○ Germanium dioxide in hydrochloric acid.
▲ Germanium tetrabromide in hydrobromide acid.
△ Germanium dioxide in hydrobromic acid.
(Solubilities expressed in grams of germanium dioxide per litre.)

Ion-exchange Experiments.—The sorptions of germanium dioxide and of chloride by Amberlite I.R.A. 400-Cl from hydrochloric acid solutions (6·5—9M) saturated with germanium dioxide or tetrachloride are given in Table 1. Outside this range of hydrochloric acid concentrations the sorption of germanium was too small to be measured by the purely chemical techniques used in this work, owing to the low solubility of the germanium (see Figure); measurable sorption of germanium occurred only when the concentration of germanium in solution was greater than *ca.* 30 mg.-atoms per l. With the solutions in hydrobromic acid, the sorption of germanium by Amberlite I.R.A. 400-Br was negligible at all acid concentrations.

TABLE 1. *Sorption of germanium and of chloride from hydrochloric acid solutions by Amberlite* I.R.A. 400-Cl (0·25 *g.*).

HCl concn. (M) *	Cl sorbed (mole per equiv. of resin)	Ge sorbed (mole per equiv. of resin)	Vol. of soln. taken (ml.)	Ratio Cl : Ge in resin phase : singly charged	doubly charged
		Germanium tetrachloride in hydrochloric acid			
6·5	1·64	0·67	10	1·9 : 1	2·9 : 1
6·5	1·25	0·595	10	1·4 : 1	2·4 : 1
7·0	1·10	0·42	50	1·2 : 1	2·2 : 1
7·0	1·34	0·485	50	1·7 : 1	2·7 : 1
7·0	1·10	0·39	5	1·3 : 1	2·3 : 1
7·5	1·25	0·39	10	1·65 : 1	2·65 : 1
7·5	1·37	0·395	10	1·9 : 1	2·9 : 1
8·0	1·10	0·15	50	1·65 : 1	2·65 : 1
		Germanium dioxide in hydrochloric acid			
8·0	1·06	0·195	50	1·3 : 1	2·3 : 1
9·0	1·05	0·08	50	1·6 : 1	2·6 : 1

* Concentration before addition of germanium dioxide or tetrachloride.

TABLE 2. *Sorption of germanium and of chloride from* 7M-*hydrochloric acid* (10 *ml.*) *by Amberlite* I.R.A. 400-Cl (0·25 *g.*) *and its dependence on time.*

Cl sorbed (mole per equiv. of resin)	Ge sorbed (mole per equiv. of resin)	Ratio Cl : Ge, singly charged	doubly charged	Time of pre-ageing (days)
1·11	0·39	1·3 : 1	2·3 : 1	1
1·17	0·415	1·4 : 1	2·4 : 1	3
1·04	0·355	1·3 : 1	2·3 : 1	9
1·04	0·34	1·3 : 1	2·3 : 1	15
1·07	0·475	1·15 : 1	2·15 : 1	43
1·37	0·46	1·8 : 1	2·8 : 1	70
1·17	0·37	1·5 : 1	2·5 : 1	300

In addition some experiments were undertaken to find if the sorption of germanium and chloride by the resin from 7M-hydrochloric acid was affected by pre-ageing of the experimental solutions (Table 2). No appreciable effect was found with pre-ageing periods of 1—300 days.

DISCUSSION

The ratios chloride : germanium in the adsorbed complexes (calculated as previously described [8]) are given in Tables 1 and 2. The low ratios found (cf. 5 : 1 for $GeCl_5^-$ or 6 : 1 for $GeCl_6^{2-}$) indicate that partly hydrolysed species, *i.e.*, $[Ge(OH)_xCl_{5-x}]^-$, or $[Ge(OH)_xCl_{6-x}]^{2-}$, are being adsorbed by the resin, the experimental results appearing to favour values of x between 3 and 4. As the sorption of germanium approaches, and in some cases exceeds, 0·5 mg.-atom per equiv. of resin, it is considered probable that it is the univalent complex which is actually taken up by the resin (cf. ref. 9).

The solubility curves obtained (Figure) show that soluble germanium complexes occur to a marked extent only in 6—9M-hydrochloric acid. It is suggested that an

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[8] Everest and Harrison, *J.*, 1957, 1439.

[9] Everest, *J.*, 1955, 4415.

equilibrium exists in these solutions between, on the one side, germanic acid or its dehydration product germanium dioxide, and, on the other side, chlorogermanate anions $GeCl_5^-$ or $GeCl_6^{2-}$, with one or more intermediate species represented by $[Ge(OH)_xCl_{5-x}]^-$. These intermediate species are the chief germanium species present in 6·5—9·0M-hydrochloric acid solutions, as is shown by the Ge : Cl ratios of the germanium chloro-complexes sorbed by the resin. Below 6·5M-hydrochloric acid hydrolysis of these intermediate species occurs with precipitation of germanium dioxide. Above 9M-hydrochloric acid chlorination of the intermediate species occurs with the formation of germanium tetrachloride as a separate phase. It is possible that chlorogermanate ions are formed initially in the latter reaction, but at the germanium concentrations used in this work the chlorogermanate ions rapidly decompose into germanium tetrachloride and chloride ions, thus explaining the decreased germanium solubilities observed with increased hydrochloric acid concentration (see Figure). Only in the sparingly soluble cæsium and rubidium hexachlorogermanates, and possibly in the very dilute solutions used by Yoshino[4] and by Nelson and Kraus,[5] do chlorogermanate ions exist as a stable or major species. However, the fact that cæsium and rubidium hexachlorogermanate can be precipitated from solutions of quadrivalent germanium in 7M-hydrochloric acid, indicates that an equilibrium concentration of chlorogermanate ions exists in these solutions, although their concentration is too low for detection by ion-exchange methods.

In the bromide system the low solubility of both germanium dioxide and tetrabromide in hydrobromic acid (see Figure), together with the negligible sorption of germanium from the solutions by ion-exchange resins, indicates that no germanium bromo-complexes are formed.

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