

*Studies in the Chemistry of Quadrivalent Germanium. Part II.\* The Depolymerisation of the Pentagermanate Ion with Change of pH, and Ion-exchange Studies of Germanate Solutions containing Sulphate and Orthophosphate.*

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An extension of the studies previously reported has shown that in solutions of pH less than 9 the pentagermanate ion is replaced by a less complex ion, probably monogermanate. This replacement proceeds to an increasing extent with fall in pH, at least down to pH 4. The less complex ion is not so firmly sorbed by anion-exchange material and is more readily displaced from it by chloride ion added to the solution than is the pentagermanate ion.

For solutions containing germanate and either sulphate or phosphate in the pH range 7—9.5 it has not proved possible to interpret the results of anion-exchange experiments in terms of the sorption of germanate ions and of sulphate or phosphate ions as such. The results are consistent, however, with the sorption of germanate ions (either mono- or penta-germanate) together with either  $[\text{GeO}_2(\text{SO}_4)]^{2-}$  or  $[\text{HGeO}_2(\text{PO}_4)]^{2-}$  ions. Evidence is thus obtained for the formation of two new complex acids of quadrivalent germanium.

THE work reported in Part I \* on the sorption of germanate ions by an anion-exchange material from solutions containing chloride has been extended and the results of similar experiments with solutions containing germanates and either sulphates or phosphates are

\* Part I, *J.*, 1954, 2438.

also reported. In these last two cases, it has not proved possible to interpret the results in terms of the sorption of sulphate (or phosphate) ions and mono- or penta-germanate ions, and the formation of complex anions is indicated. This complex-formation seems to occur over the same range of pH as the formation of pentagermanic acid, and the two reactions proceed side by side. Both species are sorbed by the exchange material, but the sorption of the pentagermanate ion occurs to a greater extent and so the sorption of germanium at the various pH values follows much the same pattern as in the experiments with chloride.

#### EXPERIMENTAL

The ion-exchange resins, the method of preparing the solutions, and the experimental procedure were all as in Part I (*loc. cit.*). It was observed, however, in one series of experiments that equilibrium was reached after the solutions and resin had been shaken mechanically for 8 hr. daily for 3 days.

*Analytical Methods.*—Sulphate was determined gravimetrically as barium sulphate after elution from the resin with 500 ml. of 2N-hydrochloric acid; excess of the eluting agent was first removed by evaporation of the solution and care was taken to avoid loss of sulphate. Phosphate was determined gravimetrically as phosphomolybdate; the resin was well washed with water to remove the bulk of the sorbed germanate before the phosphate was eluted with 2N-nitric acid (500 ml.). The amount of germanium present in the solutions used for the phosphate estimation was thus very small and it has already been shown that small quantities of germanium do not interfere in this determination (Everest, *J.*, 1953, 4117). Germanium was determined iodometrically as before (*idem, ibid.*), and chloride gravimetrically as silver chloride. The capacities of the resin samples were determined as before (Part I, *loc. cit.*).

*Results.*—*Equilibrium experiments with solutions containing chloride.* The quantities of germanium and chloride sorbed by the resin in experiments with 1.5 mmoles of germanium and 0.7 mmole of chloride present (that present as the chloride form of the resin being included) are shown in Table 1, together with the number of germanium atoms present in 1 equiv. of the germanate ions sorbed ( $=R$ ). It is apparent from these results that the values found for  $R$  lie between those previously found (Part I, *loc. cit.*) for solutions containing no added chloride and those found for solutions containing equimolecular amounts of chloride and germanium (Part I). As in the former case, the values of  $R$  fall with decrease in pH, but not to quite the same extent.

From the preceding and the present work it is clear that, at any given pH value, as the chloride concentration in the solution increases, the sorption of chloride by the exchange

TABLE 1. Sorption of germanium and chloride from solutions (75 ml.) containing 1.5 mmoles of germanium by I.R.A.-400-Cl (0.25 g.) with 0.7 mmole of total chloride present.

Soln. pH	Moles sorbed per equiv. of resin :		$R_{Ge}^*$	Method	Soln. pH	Moles sorbed per equiv. of resin :		$R_{Ge}^*$	Method
	Ge	Cl				Ge	Cl		
4.54	0.081	0.858	0.57	<i>a</i>	7.64	1.22	0.481	2.35	<i>a</i>
6.00	0.416	0.769	1.80	<i>a</i>				2.57	<i>b</i>
6.64	0.737	0.688	2.36	<i>a</i>	8.64	1.63	0.395	2.74	<i>a</i>
								2.54	<i>b</i>

\*  $R$  = No. of germanium atoms in 1 equiv. of the germanate ions sorbed; the methods of calculating  $R$  are given in Part I.

material goes up whilst that of the germanium goes down. Since exchange proceeds by equivalents, it is evident that each equivalent of chloride sorbed by the resin will displace one equivalent of sorbed germanate. Thus by comparing the changes in the amounts of germanium and chloride sorbed at corresponding pH values in the various series of experiments with differing amounts of chloride present (Fig. 1, Part I, and Table 1, Part II) values of  $R$  may be derived (called  $R'$  in Table 2 for convenience in discussion). Three sets of values have been obtained (Table 2) from the different series (the curves referred to are those of Fig. 1, Part I): (1) By method (*d*), comparison of the results given in Table 1 with corresponding results obtained by interpolation from curve *a*. (2) By method (*e*), comparison of results plotted in curves *c* and *d* with corresponding results interpolated from curve *a*. (3) By method (*f*), comparison of results from curves *c* and *d* with those in Table 1. To compare the results at corresponding pH values interpolated results have been used.

*Column experiments.* In addition to the usual batch experiments used in this work, some studies were made of the sorption of germanium from solutions passed through columns of the resin I.R.A.-400-Cl. It was assumed that the chloride liberated, and hence present in the effluent, was equivalent to the germanium sorbed (cf. method *b* for determining *R* in Part I), and mean values of *R* for the germanate ions sorbed were calculated. The results are given in Table 3. In all cases the pH of the effluent was markedly lower than that of the entering liquid.

TABLE 2. Number of germanium atoms (*R'*) in 1 equiv. of the germanate ions displaced from the resin by chloride ions at various pH values.\*

Method <i>d</i>				Method <i>e</i>				Method <i>f</i>			
pH	<i>R'</i>	pH	<i>R'</i>	pH	<i>R'</i>	pH	<i>R'</i>	pH	<i>R'</i>	pH	<i>R'</i>
4.54	0.43	7.00	1.58	6.92	1.74	9.34	2.52	7.00	2.09	7.64	2.19
6.00	1.41	7.64	1.68	7.54	1.69	9.86	2.22	7.50	2.11	8.00	2.77
6.64	1.46	8.64	2.05	8.38	1.91	10.08	1.92				
				9.00	2.61	10.42	1.58				

\* See p. 1445 for methods.

TABLE 3. Sorption of germanium from germanate solutions (75 ml.) by columns of I.R.A.-400-Cl.

Entering liquid :				Entering liquid :					
Ge (mmoles)	pH	Ge sorbed (mmoles)	Cl liberated (mmoles)	<i>R</i>	Ge (mmoles)	pH	Ge sorbed (mmoles)	Cl liberated (mmoles)	<i>R</i>
2.505	8.52	1.08	0.529	2.04	1.450	9.40	1.32	0.71	1.86
2.505	9.16	2.24	0.97	2.31	1.450	9.68	1.35	0.88	1.54

TABLE 4. Sorption of germanium and of sulphate from solutions (75 ml.) by I.R.A.-400-SO<sub>4</sub> (0.25 g.).

pH of solutions	Ge sorbed		SO <sub>4</sub> sorbed (moles/ equiv. resin)	Total equivs. sorbed in terms of :				
	moles/ equiv. resin	<i>X</i> = Ge/ <i>R</i> <sub>Ge</sub> (equivs.)		<i>X'</i> = Ge/2.5 (equivs.)	Simple ions		Complex* + sulphate (s) or germ- pentagerm-	
		<i>X</i> + SO <sub>4</sub>		<i>X'</i> + SO <sub>4</sub>	germ- anate	pentagerm- anate		
(a) 1.67 mmoles of Ge, 1.85 mmoles of sulphate present								
7.44	0.280	0.145	0.112	0.502	1.185	1.15	† 1.00 (s)	
7.80	0.503	0.234	0.201	0.428	1.09	1.06	† 1.03	
8.44	1.086	0.462	0.434	0.376	1.13	1.19	1.06	
8.94	1.467	0.587	0.587	0.316	1.22	1.22	1.09	
9.40	1.24	0.498	0.498	0.326	1.15	1.15	1.06	
(b) 1.67 mmoles of Ge, 0.65 mmole of sulphate present								
7.31	0.359	0.179	0.144	0.447	1.07	1.04	0.894 (s)	
8.34	1.289	0.555	0.516	0.364	1.28	1.24	1.17	
9.04	1.527	0.611	0.611	0.292	1.195	1.195	1.08	
9.70	1.211	0.515	0.496	0.279	1.07	1.05	1.06	
(c) 1.67 mmoles of Ge, 0.45 mmole of sulphate present								
6.91	0.175	0.094	0.071	0.471	1.04	1.01	0.94 (s)	
7.00	0.297	0.160	0.119	0.464	1.09	1.05	0.93 (s)	
7.46	0.657	0.324	0.263	0.402	1.13	1.06	1.12	
7.90	1.202	0.546	0.481	0.312	1.17	1.105	1.09	
8.62	1.402	0.572	0.561	0.300	1.17	1.16	1.06	
9.20	1.604	0.642	0.642	0.272	1.19	1.19	1.08	
9.64	1.399	0.595	0.560	0.266	1.13	1.09	1.07	
10.00	1.114	0.534	0.446	0.316	1.12	1.05	1.10	
10.40	0.707	0.399	0.283	0.350	1.10	0.98	1.20	
(d) 1.66 mmoles of Ge, 0.35 mmole of sulphate present								
6.14	0.358	0.199	0.143	0.478	1.16	1.10	† 0.96 (s)	
7.10	0.778	0.421	0.311	0.412	1.245	1.135	1.28	
8.18	1.134	0.558	0.526	0.295	1.16	1.12	1.11	
8.64	1.543	0.629	0.617	0.261	1.15	1.14	1.06	
9.10	1.642	0.657	0.657	0.259	1.175	1.175	1.07	
9.58	1.545	0.672	0.618	0.257	1.19	1.13	1.095	
10.26	1.084	0.536	0.434	0.259	1.15	0.95	1.06	
10.58	0.790	0.494	0.316	0.312	1.12	0.94	1.17	
10.86	0.380	0.316	0.152	0.347	1.01	0.85	1.47	

\* Complex ion postulated = [GeO<sub>2</sub>(SO<sub>4</sub>)]<sup>2-</sup>.

† Here there is better agreement with the ideal capacity if sorption of the complex is postulated.

*Experiments with added sulphate.* The quantities of germanium and sulphate sorbed from solutions (75 ml.) of varying pH, containing 1.5 mmoles of germanium and with 0.35, 0.45, 0.65, and 1.85 mmoles of sulphate present (as sulphate form of the resin and as sodium sulphate) are given in Table 4. In all cases the sorption of germanium reached a maximum, and that of the sulphate a minimum, at pH 9. Below *ca.* pH 6, depending on the sulphate concentration, the sorption of germanium fell to zero. At any given pH the amount of germanium sorbed decreased with increasing concentration of sulphate in the solution. It was found as before (Part I, *loc. cit.*) that the sorbed germanium could be eluted from the resin with distilled water.

*Experiments with added orthophosphate.* The quantities of germanium and phosphate sorbed by the resin from solutions (75 ml.), of varying pH, containing 1.6—1.8 mmoles of germanium and with 0.40, 1.90, and 4.15 mmoles of phosphate present (as the phosphate form of the resin and as sodium phosphate) are shown in Table 5. The sorption of germanium was again

TABLE 5. Sorption of germanium and of phosphate from solutions (75 ml.) by I.R.A.-400-PO<sub>4</sub> (0.25 g.).

pH of solutions	Ge sorbed			PO <sub>4</sub> sorbed			Total equivs. sorbed in terms of:			
	moles/ equiv. resin	X = Ge/R <sub>Ge</sub> (equivs.)	X' = Ge/2.5 (equivs.)	PO <sub>4</sub> (moles/ equiv. resin)	R <sub>PO<sub>4</sub></sub> * (moles/ equiv. resin)	Y = PO <sub>4</sub> / R <sub>PO<sub>4</sub></sub> (equivs.)	Simple Ions		Complex † + phosphate (p) or penta- germ- anate	
							X + Y	X' + Y	germ- anate	germ- anate
(a) 1.5—1.8 mmoles of Ge, 4.15 mmoles of phosphate present										
5.22	0	—	—	0.853	0.85	1.00	1.00	1.00		1.00 (p)
6.24	0	—	—	0.709	0.72	0.98	0.98	0.98		0.98 (p)
6.66	0.043	0.025	0.017	0.665	0.67	0.99	1.02	1.01		1.01 (p)
6.96	0.139	0.075	0.056	0.626	0.63	0.99	1.07	1.05		1.05 (p)
7.26	0.308	0.157	0.123	0.523	0.595	0.88	1.04	1.00		0.98 (p)
7.80	0.728	0.339	0.291	0.426	0.53	0.80	1.14	1.09		0.99 † 0.97
8.84	1.472	0.591	0.589	0.241	0.495	0.49	1.08	1.08		0.98 † 0.97
9.12	1.544	0.605	0.618	0.243	0.485	0.50	1.11	1.12		1.00 † 1.01
9.49	1.450	0.580	0.580	0.232	0.48	0.48	1.06	1.06		0.95 † 0.95
10.10	0.790	0.395	0.316	0.323	0.47	0.69	1.08	1.00		0.88 0.84
10.58	0.192	0.128	0.077	0.428	0.45	0.95	1.08	1.03		0.91 (p)
11.24	0.023	0.029	0.009	0.403	0.39	1.03	1.06	1.04		1.02 (p)
(b) 1.68 mmoles of Ge, 1.90 mmoles of phosphate present										
6.55	0.098	0.057	0.039	0.599	0.685	0.87	0.93	0.91		0.93 (p)
6.98	0.351	0.189	0.140	0.508	0.625	0.81	1.00	0.95		0.95 (p)
7.36	0.640	0.320	0.256	0.441	0.58	0.76	1.08	1.02		0.98 0.96
7.78	1.038	0.483	0.415	0.343	0.53	0.65	1.13	1.06		† 1.01 0.96
8.24	1.398	0.608	0.559	0.287	0.50	0.57	1.18	1.13		1.06 † 1.02
9.46	1.550	0.620	0.620	0.221	0.48	0.46	1.08	1.08		0.97 † 0.97
9.96	1.011	0.481	0.404	0.269	0.475	0.57	1.05	0.97		0.89 0.84
(c) 1.68 mmoles of Ge, 0.40 mmole of phosphate present										
7.09	1.128	0.594	0.451	0.406	0.615	0.66	1.25	1.11		1.19 † 1.10
8.04	1.469	0.659	0.588	0.259	0.51	0.51	1.17	1.10		1.06 † 1.00
8.99	1.833	0.727	0.733	0.160	0.49	0.33	1.05	1.06		0.98 † 0.99

\* R<sub>PO<sub>4</sub></sub> = moles of PO<sub>4</sub> sorbed per equiv. of resin under the same conditions, but in the absence of germanium. When pH of solutions was less than 7 some phosphate was eluted from resin on washing; this was determined in both cases (*i.e.*, Ge present and Ge absent) and the appropriate corrections made.

† Here there is better agreement with the ideal capacity if sorption of the complex ion is postulated.

‡ Complex ion postulated = [HGeO<sub>2</sub>(PO<sub>4</sub>)]<sup>2-</sup>.

greatest at pH 9.0—9.2, but, whilst that of phosphate passed through a minimum at this point, there was an overall trend towards a lower degree of sorption with rise of pH. That this last was due to progressive sorption of HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> ions in place of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, is apparent from the blank experiments carried out with phosphate alone (see footnote to Table 5). As before, the germanium sorbed by the resin could be eluted with distilled water.

## DISCUSSION

*Experiments with Added Chloride.*—The values of R given in Table 1, taken in conjunction with those previously reported (Part I) for solutions with no added chloride, indicate the sorption below pH 9 by the exchange material of a lower polymer or of the

monomer of the germanate ion together with the pentagermanate ion. It is evident that the less complex acid is sorbed to an increasing extent as the pH is lowered, and this behaviour is consistent with a progressive depolymerisation of the pentagermanate ion. Further evidence is provided by the values of  $R'$  quoted in Table 2. As pointed out in Part I, no evidence has yet been forthcoming to show that intermediate polymeric ions such as  $\text{Ge}_4\text{O}_9^{--}$  or  $\text{Ge}_2\text{O}_5^{--}$  exist in solutions in this range of pH, and it is concluded that the less complex ion formed is in fact the monogermanate ion—a conclusion in agreement with the views of Souchay (*Bull. Soc. chim.*, 1953, 395) and of Schwarz and Huf (*Z. anorg. Chem.*, 1931, 203, 395).

Some further support for such a change in the extent of polymerisation of the germanate ion with pH is provided by the recent observation by Tchakarian and Wallace (*Bull. Soc. chim.*, 1954, 1067) that a precipitate of thallos pentagermanate could be obtained on mixing a thallos nitrate solution (1%) with a germanium dioxide solution (0.04M) only if the pH of the solution was raised by addition of ammonia.

Although they were based on experiments in which equilibrium conditions were not reached—and hence are not so readily interpreted—the results quoted for the column experiments in Table 3 provide, albeit qualitatively, still further evidence for the sorption of a less complex germanate ion than the pentagermanate.

It is apparent from the results given in Part I and in Tables 1 and 2 that the values found for  $R$  (and  $R'$ ) at a given pH (in the range 4–9) increase with the concentration of chloride in the solutions—thus the values of  $R'$  determined by the method *f* are significantly higher than those determined by methods *d* or *e* (Table 2). Hence, it may be concluded that the monogermanate ions are more readily displaced from the resin by chloride ions than are the pentagermanate ions. This probably arises, at least partly, from the fact that monogermanic acid is the weaker acid, since at pH values above 9, where this acid would be more fully ionised, the effect of the presence of chloride is less marked.

*Experiments with Added Sulphate and Orthophosphate.*—Attempts have been made to account for the capacity of the resin samples used in terms of the sorption of germanate ions and either sulphate or phosphate ions (Tables 4 and 5). In calculating the equivalents of germanate sorbed, two extreme possibilities have been considered, *viz.*, (1) that the germanium is sorbed as a mixture of mono- and penta-germanate ions in the same ratio as by the hydroxide form of the resin from solutions of the same pH but containing no other anions (as reported in Part I), the equivalents of germanate sorbed then being given by  $X = (\text{moles of Ge sorbed per equiv.})/R_{\text{Ge}}$ ; and (2) that the germanium is sorbed entirely as pentagermanate, the equivalents so sorbed being given by  $X' = (\text{moles of Ge sorbed per equiv.})/2.5$ . The results of the experiments in which chloride ion was present have already indicated that the correct value to be employed—which depends on the value of  $R$  to be used when a second anion is present—will be between those given by  $X$  and by  $X'$ .

It has been assumed that the sulphate ion was sorbed as the  $\text{SO}_4^{--}$  ion over the pH range studied here, but in the case of phosphate it proved necessary to take into account the effect of pH on the species sorbed, and this has been determined in a series of blank experiments over the same ranges of pH and phosphate concentration, but with no germanium present (giving the values of  $R_{\text{PO}_4}$ ; Table 5).

From the results of the calculations, which are given in Tables 4 and 5, it is evident that the capacities calculated in this way [ $(X + \text{SO}_4)$  or  $(X' + \text{SO}_4)$  and  $(X + Y)$  or  $(X' + Y)$ ] are in good agreement (*i.e.*, within  $\pm 5\%$ ) with the ideal value of 1 equiv. sorbed per equiv. of resin for pH values below 7 and over 9 or 10. Between pH 7 and about pH 9 a significant deviation from the ideal value is found, but in this range the capacities may be accounted for by assuming instead the sorption of the complex ions  $[\text{GeO}_2(\text{SO}_4)]^{--}$  or  $[\text{HGeO}_2(\text{PO}_4)]^{--}$ , together with free germanate, sulphate, or phosphate. The method of calculating the capacities in this case follows closely that employed by Jameson and Salmon (*J.*, 1954, 4013).

Of all the possible complexes that can be formed between sulphate and mono- and penta-germanate ions only the  $[\text{GeO}_2(\text{SO}_4)]^{--}$  ion accounts satisfactorily for the resin capacities. The number of complexes which can be formed between the tribasic phosphoric acid and the various germanic acids is high, and products are acids of potentially high

basicity, so the number of possible ions that may be sorbed is great. However, the assumption of the sorption of ions derived from pentagermanic acid {*e.g.*,  $[\text{Ge}_5\text{O}_{10}(\text{PO}_4)]^{3-}$  or  $[\text{Ge}_5\text{O}_4(\text{PO}_4)_7]^{9-}$ } does not lead to satisfactory values for the resin capacity. Thus, a complex derived from monogermanic acid seems to be indicated, and by analogy with the germanate-sulphate system a 1 : 1 complex might be expected. The postulation of the sorption of the  $[\text{HGeO}_2(\text{PO}_4)]^{2-}$  ion does in fact make it possible to account satisfactorily for the resin capacity in the pH range where the sorption of simple ions does not.

The fact that the complex-formation between monogermanic acid and sulphate or phosphate ion occurs over essentially the same pH range as the condensation of monogermanic acid to give pentagermanic acid, suggests that both processes are favoured by the same conditions. In fact, both appear to proceed side by side, for the sorption of both complexes appears to be accompanied by the sorption of free germanate, as pentagermanate (Tables 4 and 5). It thus appears that in this pH range monogermanic acid can condense with other oxy-anions as well as with itself. The extent to which condensation occurs with a second oxy-anion (not germanate) seems to be limited, however, and does not appear to proceed to a stage comparable with the formation of the pentagermanate ion.

Since, in our experiments, a large proportion of the germanium initially present in solution was sorbed by the exchange material—owing to the comparatively low solubility of germanium dioxide and the high sorption of germanium on the resin—and since the resin may show some selectivity towards sorption of the complex ions, it is not possible to assess, even qualitatively, the extent to which the complexes are formed in the solutions. Nevertheless, the fact that the sorption of such complexes occurs at all throws new light on the complex chemistry of quadrivalent germanium.

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