Studies in the Chemistry of Quadrivalent Germanium. Part III.* Ion-exchange Studies of Solutions containing Germanium and Oxalate.

By D. A. Everest.

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The results of anion-exchange studies on germanate solutions in presence of oxalates above pH 7 are interpreted in terms of the sorption of penta- and mono-germanate ions and of oxalate ions. These results confirm the conclusions reached in Parts I and II * concerning the pH dependence of the formation and degradation of the pentagermanate ion.

Although above pH 7 no complex ions could be detected, below pH 6 the ion-exchange data indicate that complex germanium-oxalate ions are being sorbed by the exchanger. Below *ca.* pH 3 the germanioxalate ion, $[Ge(C_2O_4)_3]^{2-}$, appears to be the chief species sorbed, whilst from pH 3 to 6, $[GeO(C_2O_4)_2]^{2-}$ and $[GeO_2(C_2O_4)]^{2-}$ ions are mainly taken up by the exchanger. Further evidence for the existence of the last two ions has been given by anion-exchange studies on germanate solutions containing insufficient oxalate to convert all the germanium into $[Ge(C_2O_4)_3]^{2-}$ ions.

The formation of a complex germanic oxalate was first observed by Bardet and Tchakarian (*Compt. rend.*, 1929, **189**, 914) on dissolving germanium dioxide in oxalic acid solution. Although they did not isolate free germanioxalic acid, measurements of the oxalic acid : germanium ratio in solution led them to assign the formula $H_2Ge(C_2O_4)_3$ to the complex. Germanium dioxide was also found to be highly soluble in solutions of ammonium hydrogen oxalate; evaporation of these solutions gave only thick uncrystallisable syrups from which no solids could be isolated. Determination of the oxalate : germanium ratio led Bardet and Tchakarian to suggest the presence in these syrups of the compound $Ge(C_2O_4)_2,GeO(C_2O_4),xH_2O$. Further evidence for the existence of germanioxalic acid, $H_2Ge(C_2O_4)_3$, has been obtained by Tchakarian [*Compt. rend.*, 1937, **204**, 356; *Ann. Chim.* (*France*), 1939, **12**, 415] and by Willard and Zuehlke (*Ind. Eng. Chem. Anal.*, 1944, **16**, 322) through their isolation of salts of this acid with quinine, strychnine, and 5 : 6-benzoquinoline. Tchakarian also showed that germanic oxalate complexes were sufficiently stable not to be decomposed by hydrogen sulphide, and he applied this fact in devising a method for the extraction of germanium from germanite.

If in germanioxalic acid the three oxalate groups are arranged octahedrally around the central germanium atom, it should be possible to resolve this complex into optically active forms. This was demonstrated by Moeller and Nielsen (*J. Amer. Chem. Soc.*, 1953, **75**, 5106) through the fractional crystallisation of the quinine salt described by Tchakarian (*loc. cit.*). In aqueous solution the free acid racemised, all activity being lost after 40 hr. These authors also obtained qualitative evidence for the occurrence of the $[Ge(C_2O_4)_3]^{2-}$ ion in the quinine salt by *X*-ray powder photographs.

Further evidence for the complex character of solutions of quadrivalent germanium in oxalate media has been furnished by Douvillé, Duval, and Lecompte (*Compt. rend.*, 1941, **212**, 697) and by Everest (*J.*, 1953, 4117). The former showed that the infrared spectra of such solutions had features characteristic of the spectra given by solutions of complex oxalates as a class. Everest showed that in presence of oxalates quadrivalent germanium was not reduced to the bivalent state by hypophosphorous acid, although this reduction occurred readily in less strongly complex-forming media.

In view of the utility of ion-exchange methods in elucidating the nature of simple germanate solutions (Everest and Salmon, Part I, *loc. cit.*) and in detecting the existence of the complex anions $[GeO_2(SO_4)]^{2-}$ and $[HGeO_2(PO_4)]^{2-}$ (*idem*, Part II, *loc. cit.*), it was considered that similar studies on solutions of germanium dioxide in oxalate media would throw new light on the formation, type, and stability limits of the germanic oxalate complexes.

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* Parts I and II, *J.*, 1954, 2438; 1955, 1444.

EXPERIMENTAL

Solutions.—Stock solutions were prepared by dissolving pure germanium dioxide in boiled-out distilled water; these solutions contained 28—29 mmoles of germanium per l. The pH and the oxalate concentration of the solutions were varied by addition of oxalic acid, sodium oxalate, or sodium hydroxide. The solutions, containing a known amount of germanium (1·3—1·4 mmoles), were diluted to 75 ml. before addition of resin.

Anion-exchanger.—Analytical-grade Amberlite IRA-400 (supplied in the hydroxide form) was used throughout (in 0·25-g. samples) after conversion into the oxalate form, obtained by stirring the hydroxide form with excess of *ca.* 0·5N-oxalic acid, washing the resin by decantation, stirring it with successive portions of distilled water (time of contact 24 hr. with each portion), and finally air-drying it. Thus prepared, the resin lost a minimum of oxalate by hydrolysis during washing.

Equilibrium Experiments and Analytical Methods.—A period of 12—14 days was allowed for equilibrium between the solution and the resin phase to be established, at least 24 hours' mechanical shaking being included in this period. The separation of the solution and the resin phase, the estimation of the germanium sorbed by the resin, and the measurement of the pH of the solutions and of the capacities of the various resin samples were all carried out as in Part I (*loc. cit.*). The oxalate sorbed on the resin was eluted with 500 ml. of 3N-sulphuric acid during 48 hr. and then determined in the eluate by titration with standard potassium permanganate.

Results.—The quantities of germanium and of oxalate sorbed by the resin from solutions (75 ml.) of varying pH containing 1·2—1·4 mmoles of germanium and with 1·35, 2·85, and 5·35 mmoles of oxalate present are shown in Tables 1 (pH values above 7) and 2 (pH values below 7). A few values for germanium sorptions only, with 0·35 mmole of oxalate present, are also given in Table 1. At pH 4·5, or less, the amount of germanium sorbed reached a nearly constant value of 0·5—0·6, and that of the sorbed oxalate 1·4—1·6, moles per equiv. of resin (Table 2). Above pH 7 (Table 1) the germanium and oxalate sorptions followed the same course as did those of germanium and chloride (obtained in parallel experiments) reported in Parts I and II (*locc. cit.*); the amount of germanium sorbed reaching a maximum, and that of the oxalate a minimum, at pH 9·0—9·2. Between pH 6 and 7 the sorption of germanium by the exchanger fell nearly to zero, whilst that of the oxalate approached the value required for saturation of the resin with simple oxalate ions (Table 2). A maximum of *ca.* 50% of the germanium initially present in solution (with 1·35 and 2·85 mmoles of oxalate present) was sorbed by the resin at pH 9·0—9·2; with only 0·35 mmole of oxalate present this value was increased to *ca.* 80%. Below pH 4, with 2·85 and 5·35 mmoles of oxalate present, the maximum sorption was *ca.* 25%.

In control experiments it was found that, with 2·85 mmoles of oxalate in 75 ml. solution, the moles of oxalate sorbed per equiv. of resin (R_{0x}) varied from 0·54 at pH 4·9 to 0·82 at pH 1·9. Above pH 6 only $C_2O_4^{2-}$ ions were sorbed by the resin.

DISCUSSION

Experiments at pH *Values above* 7.—The results obtained in this pH region (Table 1) confirm the conclusions reached in Parts I and II (*locc. cit.*) that the maximum in the germanium sorption at pH 9·0—9·2 is due to the uptake of pentagermanate ions by the resin, and that the decrease in the germanium sorption on either side of pH 9·0—9·2 results from the progressive degradation of pentagermanate ions into monogermanate. By the method of calculation described in Part II it has been possible to account quantitatively for the capacity of the resin samples used in terms of the sorption of mono- and penta-germanate ions and of oxalate ions. This is illustrated by the closeness of the values in the columns ($X + C_2O_4$) and ($X' + C_2O_4$) of Table 1 to the ideal value of one equiv. sorbed per equiv. of resin.

No evidence has been found for the sorption of any complex germanium–oxalate ions above pH 7. This is in contrast to the behaviour of solutions of germanates in presence of sulphate or phosphate (Part II), where, under conditions similar to those occurring in the present work, the complex anions $[GeO_2(SO_4)]^{2-}$ and $[HGeO_2(PO_4)]^{2-}$ were sorbed by the resin between pH 7 and 9·5. It is noteworthy that Willard and Toribara (*J. Amer. Chem. Soc.*, 1942, **64**, 1749) found that no combination occurred between quadrivalent tin and oxalate in alkaline media.

Experiments at pH *Values below* 7.—The increase in the germanium sorption from nearly zero at pH 6 to *ca.* 0·5 mole per equiv. of resin below pH 4·5, together with the parallel increase in oxalate sorption, is direct evidence for the presence of sorbable germanium oxalate complexes in solution. By comparison, in the germanium–chloride system (Part I)

TABLE 1. *Sorption of germanium and of oxalate from solutions* (75 *ml.*) *at* pH *values above* 7 *by* IRA-400-C_2O_4 (0·25 *g.*).

pH of soln.	Germanium sorbed: * moles per equiv. of resin	Germanium sorbed: * X = Ge/R_{Ge} (equiv.)	Germanium sorbed: * X′ = Ge/2·5 (equiv.)	Oxalate sorbed, moles per equiv. of resin	Simple ions X + C_2O_4	Simple ions X′ + C_2O_4
(*a*) 1·320 Mmoles of germanium, 2·85 mmoles of oxalate present						
7·78	0·190	0·067	0·056	0·468	1·00	0·99
8·26	0·391	0·170	0·156$_5$	0·398	0·98	0·95
8·84	0·685	0·274	0·274	0·383	1·04	1·04
9·00	0·732	0·293	0·293	0·358	1·01	1·01
9·32	0·858	0·343	0·343	0·347	1·04	1·04
9·74	0·740	0·322	0·296	0·350	1·02	1·00
10·02	0·504	0·240	0·202	0·392	1·02	0·99
10·26	0·202	0·101	0·081	0·412$_5$	0·93	0·91
(*b*) 1·320 Mmoles of germanium, 1·35 mmoles of oxalate present.						
7·40	0·151	0·075	0·056	0·475	1·03	1·01
7·80	0·347	0·158	0·139	0·441	1·04	1·02
8·46	0·575	0·243	0·228	0·378	1·00	0·98
9·06	0·803	0·321	0·321	0·367	1·05	1·05
9·42	0·828	0·345	0·331$_5$	0·348	1·04	1·03
9·62	0·730	0·319	0·293	0·398	1·19	1·09
(*c*) 1·45 Mmoles germanium, 0·35 mmole of oxalate present.						
5·10	0·065	—	—	—	—	—
7·24	0·539	—	—	—	—	—
8·36	1·340	—	—	—	—	—
9·14	1·460	—	—	—	—	—
9·76	1·380	—	—	—	—	—
10·12	0·982	—	—	—	—	—

* X and X′ are defined in Part II (*loc. cit.*).

TABLE 2. *Sorption of germanium and of oxalate from solutions* (75 *ml.*) *at* pH *values below* 7 *by* IRA-400-C_2O_4 (0·25 *g.*).

pH of soln.	Species sorbed (moles per equiv. of resin) Ge	Species sorbed (moles per equiv. of resin) oxalate	Ratio moles oxalate : moles Ge on resin	Ions sorbed by resin
(*a*) 1·395 Mmoles of germanium, 5·35 mmoles of oxalate. Ratio oxalate : germanium in solution = 4·82.				
6·80	0·034	0·519	15·3	$C_2O_4^{2-}$, $[GeO_2(C_2O_4)]^{2-}$, and $[GeO(C_2O_4)_2]^{2-}$
5·56	0·230	0·598	2·6	
5·28	0·337	0·792$_5$	2·35	
4·84	0·471	0·951	2·02	$[GeO(C_2O_4)_2]^{2-}$
4·42	0·507	1·052	2·08	
3·96	0·493	1·065	2·16	
3·42	0·510	1·347	2·64	Mainly $[Ge(C_2O_4)_3]^{2-}$
3·00	0·510	1·434	2·81	
2·54	0·508	1·460	2·87	
2·04	0·536	1·511	2·82	
1·76	0·553	1·558	2·82	
1·58	0·543	1·564	2·88	
1·46	0·545	1·524	2·80	
(*b*) 1·320 Mmoles of germanium, 2·85 mmoles of oxalate. Ratio oxalate : germanium in solution = 2·04.				
6·60	0·060	0·510	8·5	$C_2O_4^{2-}$, $[GeO_2(C_2O_4)]^{2-}$, and $[GeO(C_2O_4)_2]^{2-}$
5·66	0·171	0·648	3·8	
5·18	0·282	0·735	2·61	
4·78	0·450	0·929	2·06	
4·40	0·564	0·955	1·69	
4·38	0·545	1·038	1·91	
3·36	0·629	1·263	2·01	Mainly $[GeO(C_2O_4)_2]^{2-}$ with some $[Ge(C_2O_4)_3]^{2-}$
2·22	0·597	1·470	2·46	
2·02	0·666	1·446	2·17	
1·86	0·603	1·481	2·45	

where no complexing occurs under conditions closely related to those in the present work, the sorption of germanium tended to zero below pH 6. The sorption of oxalate in presence of germanium (Table 2) is also greater, at any pH value below 6, than that required for saturation of the resin with simple oxalate ions.

In the experiments at the higher oxalate concentration (oxalate : germanium ratio in solution 4·82, Table 2) the resin, below pH 3, appears to be nearly saturated with a complex anion containing 3 moles of oxalate to one of germanium, as is illustrated by the value of *ca.* 2·85 for the ratio of oxalate to germanium in the resin phase (Table 2). This complex is probably the bivalent germanioxalate ion, $[Ge(C_2O_4)_3]^{2-}$, the existence of which has been indicated by the work of Bardet and Tchakarian, Tchakarian, Willard and Zuehlke, and Moeller and Nielsen (*locc. cit.*). The closeness of the amount of germanium sorbed to 0·5 mole per equiv. of resin is consistent with the sorption of a bivalent ion. A small amount of a univalent ion, such as $[HGe(C_2O_4)_3]^-$ or $[HGeO(C_2O_4)_2]^-$ (see below) may also be sorbed below pH 2 where the amount of germanium on the resin rises slightly over 0·5 mole per equiv. of resin.

From pH 3 to 4·5 the ratio of oxalate to germanium in the resin phase falls from 2·85 to 2 (Table 2). A bivalent ion is still taken up by the resin in this pH region, however, as the amount of germanium sorbed remains approximately constant at 0·5 mole per equiv. of resin. These two facts can be accounted for by assuming the sorption of increasing quantities of a complex ion such as $[Ge(OH)_2(C_2O_4)_2]^{2-}$ or $[GeO(C_2O_4)_2]^{2-}$. Sorption of small amounts of such an ion would account for the slightly low oxalate : germanium ratio (2·8—2·9) in the resin phase below pH 3 where $[Ge(C_2O_4)_3]^{2-}$ ions are considered to be the chief species sorbed.

The rapid decrease in the amounts of germanium and oxalate sorbed by the exchanger between pH 4·4—4·8 and 6·8, in both the higher and the lower oxalate concentration series (Table 2), indicates that decomposition of the germanium–oxalate complexes occurs in this pH range. This range is close to the pH value of 5·2 at which Willard and Toribara (*loc. cit.*), by means of pH titrations, found that solutions of quadrivalent tin in oxalate media decomposed to give hydrated stannic oxide. The increase in the ratio of oxalate to germanium in the resin phase observed between pH 4·4 and 6·8 (Table 2) is due, not to sorption of complexes with an increased oxalate : germanium ratio, but to the replacement of complex ions on the resin by oxalate ions. This is confirmed by the parallel decrease observed in the amount of germanium sorbed by the resin.

By using Jameson and Salmon's method of calculation (*J.*, 1954, 4013), attempts were made, between pH 4·8 and 6·8, to account for the capacity of the resin samples used in terms of the sorption of oxalate ions and either $[GeO(C_2O_4)_2]^{2-}$ or $[GeO_2(C_2O_4)]^{2-}$ ions alone. These attempts failed, the former possibility giving low results for the capacity, and the latter high ones. Probably it is a mixture of these two ions, together with free oxalate, which is actually sorbed by the resin in this pH range. This mixture would contain mainly $[GeO(C_2O_4)_2]^{2-}$ ions at pH 4·8 and $[GeO_2(C_2O_4)]^{2-}$ ions at pH 5·56.

In the experiments at the lower oxalate concentration (oxalate : germanium ratio in solution 2·04, Table 2) it is not possible for all the germanium in solution to be converted into $[Ge(C_2O_4)_3]^{2-}$ ions, and the conditions are those favourable to the existence of $[GeO(C_2O_4)_2]^{2-}$ ions. In fact, below pH 4·4 (Table 2), principally $[GeO(C_2O_4)_2]^{2-}$ ions appear to be taken up by the exchanger, although the increase in the ratio of oxalate to germanium in the resin phase below pH 3 indicates that some $[Ge(C_2O_4)_3]^{2-}$ ions are then also being sorbed. The increase in the amount of germanium sorbed over 0·5 mole per equiv. of resin is more marked in the lower oxalate concentration series than in the higher one. This is possibly caused by the weaker acidic character of $H_2[GeO(C_2O_4)_2]$ as compared with $H_2[Ge(C_2O_4)_3]$, which causes sorption of some univalent $[HGeO(C_2O_4)_2]^-$ ions as the pH of the solution decreases.

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