

*Studies in the Chemistry of Quadrivalent Germanium: Ion-exchange
Studies of Solutions of Germanates.*

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[Reprint Order No. 5066.]

Anion-exchange studies with a strongly basic exchanger show that, at pH values close to 9, germanium, in the form of the pentagermanate ion, is strongly adsorbed from germanate solutions, even in the presence of comparable concentrations of chloride. At both lower and higher pH values the adsorption of germanium falls off rapidly and in such a manner as to indicate a decrease in the concentration of pentagermanate ions in the solutions. From solutions with higher pH values, less polymerised (probably monogermanate) ions are adsorbed in place of the pentagermanate ions. In neutral and slightly acidic solutions, too, there is evidence, although less conclusive, of adsorption of a monomeric germanate ion.

The removal of adsorbed germanium from the resin on washing is interpreted as involving, as a first stage, the hydrolysis of the strongly adsorbed pentagermanate ion to the less strongly adsorbed monogermanate ion.

THE chemical nature of germanium dioxide in solution over the pH range 4—13 has received considerable attention. The results of a series of pH titrations of germanium dioxide solutions of various concentrations with alkali have been interpreted as indicating the presence of the pentagermanate ion $\text{Ge}_5\text{O}_{11}''$ in solutions in the pH range 8.8—9.2. This is the region of the "isohydric point"—the point of intersection of the pH titration curves corresponding to the various concentrations of germanium dioxide. At higher pH values depolymerisation of the pentagermanate ion to the monogermanate ion, HGeO_3' ,

was said to occur (Carpeni and Tchakarian, *Compt. rend.*, 1948, **226**, 725; Carpeni, *Bull. Soc. chim.*, 1948, 629). The isolation of crystalline potassium pentagermanate from a solution of germanium dioxide in 2M-potassium chloride at pH 9.2 (Tchakarian and Carpeni, *Compt. rend.*, 1948, **226**, 1094) lent support to the view that the pentagermanate ion was present in such solutions. Some of Carpeni's conclusions have been criticised by Souchay and others (Souchay and Teyssèdre, *Bull. Soc. chim.*, 1951, 938; Bye, *ibid.*, 1953, 390; Souchay, *ibid.*, p. 395). For instance, while Carpeni (*ibid.*, 1952, 1010; *loc. cit.*) believed that pentagermanic acid was the principal species present in pure germanium dioxide solutions, Souchay, who quoted and extended Roth and Schwartz's cryoscopic data (*Ber.*, 1926, **59**, 338), used these to support his view that monogermanic acid was present in such solutions and that this underwent first polymerisation to pentagermanate and then depolymerisation to monogermanate again with rise of pH.

Schwarz and Huf (*Z. anorg. Chem.*, 1931, **203**, 188) have interpreted the results of their dialysis experiments with solutions of germanium dioxide in aqueous potassium nitrate as showing the presence of a monomeric species below pH 5.5, of an increasing amount of pentagermanic acid between pH 5.5 and 8.4, and of monogermanate ion above pH 12.5. Between pH 8.8 and 12.5 these workers could get no useful results as a precipitate [considered by Tchakarian and Carpeni (*loc. cit.*) to be potassium pentagermanate] was formed on the membrane. Similar experiments by Brintzinger (*Z. anorg. Chem.*, 1948, **256**, 98) also indicated the presence of monogermanate ions in strongly alkaline media (pH >13).

The fact that germanium dioxide is soluble in water as well as in acid and alkaline solutions suggested that ion-exchange studies would provide a convenient method of determining the nature of the ions present in solution at various pH values—both in the presence and in the absence of other anions. Preliminary experiments showed that germanium was not adsorbed by the cation-exchanger Zeo-Karb 225 (in the hydrogen form) from solutions in the pH range 1—7, thus indicating the absence in them of germanium cations. Germanium was adsorbed, however, by the strongly basic anion-exchanger Amberlite I.R.A.-400 (in the hydroxide and the chloride form) from solutions with pH values in the range 4—13, even in the presence of comparable concentrations of chloride. Determinations of the quantities of the various species adsorbed and of the capacities of the resin samples used have permitted the determination of the ionic form in which the germanium is adsorbed at the various pH values.

EXPERIMENTAL

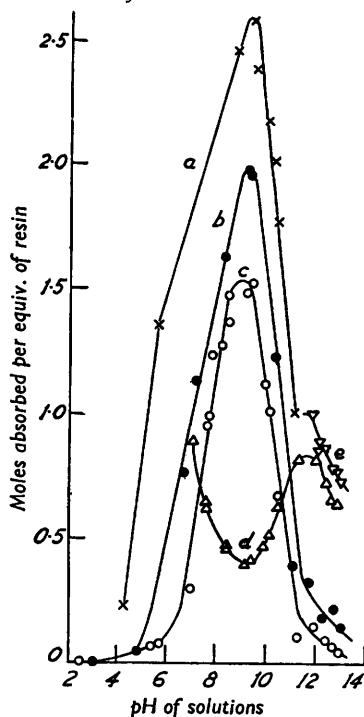
Solutions.—Stock solutions were prepared by dissolving pure germanium dioxide in boiled-out distilled water. These solutions contained 31—33 mmoles of germanium per l. [*i.e.*, in the range of stable concentrations (Gulzian and Muller, *J. Amer. Chem. Soc.*, 1932, **54**, 3142; Schwarz and Huf, *loc. cit.*)]. The pH of the solutions was raised by addition of sodium hydroxide and lowered by addition of hydrochloric acid. Chloride was added as sodium chloride. The solutions, containing a known amount of germanium (1.6—1.8 mmoles), were diluted to 75 ml. before addition of the resin.

Anion-exchanger.—Analytical-grade Amberlite I.R.A.-400 (supplied in the hydroxide form) was used throughout (0.25-g. samples) in either the hydroxide or the chloride form. The latter was obtained from the former by treatment with 2N-hydrochloric acid and was washed free from excess of acid and dried in the air before use.

Equilibrium Experiments.—At least 18 days, with frequent shaking, were allowed for equilibrium between solution and resin phases to be established (experiments extending over longer periods established that this was adequate). The solution was then filtered through a dry column (1 cm. internal diameter, 10 cm. long above the sealed-in sintered-glass disc of No. 2 grade porosity). The filtrate was retained, and aliquot portions of it were used for analysis and pH measurements. The resin was then transferred to the column and washed rapidly with water (*ca.* 50 ml.) under suction. In this way any solution adhering to the resin was quickly displaced and interaction between partly diluted solution and the resin was avoided. Very little of the adsorbed germanium was removed at this stage (see below) and these washings were rejected. After the column had been filled with water, a further 300—500 ml. of water were slowly passed through it to complete the washing. Since in this process

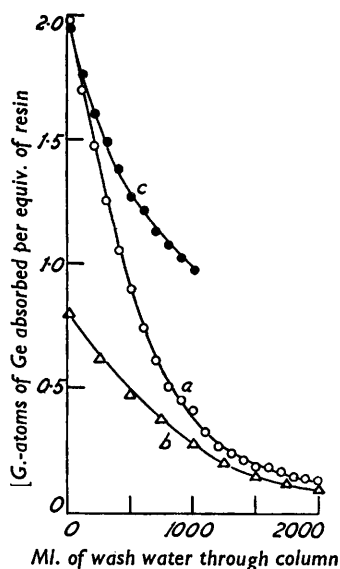
part of the germanium on the resin was displaced, the amount of this originally adsorbed was determined from the difference in germanium content in the original solution and in the filtrate. Any chloride adsorbed by the resin was then removed by elution with 500 ml. of 3*N*-nitric acid and determined in the eluate (the elution also removed the remainder of the germanium adsorbed). After being washed, the resin was converted completely into the chloride form by treatment with 500 ml. of 3*N*-hydrochloric acid and then washed until free from excess of acid. A final elution with 3*N*-nitric acid and a determination of the chloride thus removed gave the capacity of the resin sample. As this varied from sample to sample, the results have been expressed in terms of moles adsorbed per equiv. of resin.

FIG. 1. Adsorption of germanium and chloride by I.R.A.-400.



Mmoles added Ge	Cl	Resin form	Adsorbed on resin Ge	Cl
1.6—1.8	0—0.3	OH	× a	—
1.6—1.8	0.8—1.0	Cl	● b	—
1.6—1.8	1.8	Cl	○ c	△ d
0	1.8	Cl	—	▽ e

FIG. 2. Removal of germanium from I.R.A.-400 on washing.



Elution with distilled water ○ a; △ b
Elution with water from mixed-bed resin
column ● c

Analytical Methods.—Germanium was estimated iodometrically, after reduction to the bivalent state (Everest, *J.*, 1953, 4117). Chloride was determined gravimetrically as silver chloride. Measurements of pH were made with a commercial-type pH meter, a glass electrode and a saturated calomel electrode being used. For strongly alkaline solutions a Cambridge Instrument Company "Alki" glass electrode was used.

RESULTS.—Equilibrium experiments. The quantities of germanium and chloride adsorbed by the resin in experiments with equimolecular quantities of germanium and chloride present (chloride added as the chloride form of the resin being included) are represented in Fig. 1 (curves *c* and *d*). The adsorption of germanium passes through a maximum at a pH of 9.0—9.2, a minimum in the adsorption of chloride occurring at the same point. The rapid decrease in adsorption of germanium on either side of this peak is accompanied by a marked increase in adsorption of chloride. Above pH 12 the adsorptions of both germanium and chloride decrease as a result of competitive adsorption of hydroxide. The starting point and extent of this competition are apparent from the results of blank experiments with chloride only present

which are also shown in Fig. 1. Above a pH value of 12 the amounts of chloride adsorbed fall below the value of 1 mole per equiv. of resin and the differences found indicate the moles of hydroxide ion adsorbed.

With half the amount of chloride or with no chloride present—except for traces, added as hydrochloric acid, to obtain solutions of low pH—the adsorption of germanium is higher at all pH values, particularly in the latter case. However, the shape of curves (*a* and *b* in Fig. 1) is substantially the same and the peak occurs at the same point.

Hydrolysis of the germanate form of Amberlite I.R.A.-400. As already mentioned (p. 2439), washing the resin resulted in the slow removal of the germanium adsorbed. The rate of removal depended to some extent on the rate of flow of the wash water, but when this was about 100 ml. per hr. 2 l. of water removed approximately 1 mmole of germanium from 0.25 g. of resin. The results of experiments in which every 100-ml. or 250-ml. fraction of the washings was collected and analysed for germanium content are shown in Fig. 2. It can be seen that the rate of desorption of germanium was markedly less if the distilled water used for washing was first passed through a column of Bio-Demineralit (mixed-bed) resin and care taken to exclude the carbon dioxide of the atmosphere.

When the resin was left in contact with a fixed amount of water, the amount of germanium adsorbed fell rapidly at first, then more slowly, and finally reached a constant value (Table 1).

TABLE 1. *Rate of desorption of germanium from Amberlite I.R.A.-400 (0.25 g. of chloride- and germanate-form) on contact with water (250 ml.) at room temperature.*

Time (hr.)	0	4	30	100	480	1150	1680
Ge on resin (mmoles)	1.35	1.21	1.09	0.99	0.90	0.84	0.84 *

* pH of aqueous phase = 7.56.

The number of germanium atoms present in one equivalent of the germanate ions adsorbed. If the results of the equilibrium experiments are expressed in terms of moles adsorbed per equiv. of resin, then the number of germanium atoms present in one equiv. of the germanate ions adsorbed (= *R*) may be found in the following ways :

$$(a) R = (\text{moles of Ge adsorbed}) / (1 - \text{equivs. of other species adsorbed}).$$

When hydroxide is one of the species adsorbed it has to be determined indirectly and this has to be done in two ways (Table 2).

TABLE 2. *The number of germanium atoms present in one equivalent of the germanate ions adsorbed (R).*

pH	R	Method *	pH	R	Method *	pH	R	Method *
(1) I.R.A.-400-(OH), 1.8 mmoles of Ge, 0—0.3 mmole of Cl.								
4.24	0.58	<i>a</i>	9.36	2.59	<i>a</i>	10.22	2.02	<i>a</i>
5.56	1.69	<i>a</i>	9.41	2.39	<i>a</i>	10.37	1.77	<i>a</i>
7.45	2.03	<i>a</i>	9.93	2.18	<i>a</i>	11.03	1.00	<i>a</i>
8.68	2.46	<i>a</i>						
(2) I.R.A.-400-(Cl), 1.66 mmoles of Ge, 0.7—0.9 mmole of Cl.								
7.71	2.31	<i>b</i>	7.71	2.30	<i>a</i>	9.10	2.59	<i>c</i>
9.20	2.66	<i>b</i>						
(3) I.R.A.-400-(Cl), 1.8 mmoles of Ge, 1.8 mmoles of Cl.								
6.92	2.69	<i>a</i>	9.12	2.44	<i>a</i>	11.28	0.57	<i>a</i>
7.52	2.68	<i>a</i>	9.34	2.53	<i>a</i>	11.96	0.81	<i>a</i>
7.74	2.66	<i>a</i>	9.86	2.11	<i>a</i>	12.34	0.68 † 0.56 ‡	<i>a</i>
8.38	2.73	<i>a</i>	10.08	2.09	<i>a</i>	12.66	0.49 † 0.38 ‡	<i>a</i>
8.38	2.57	<i>a</i>	10.42	1.77	<i>a</i>	12.84	0.39 † 0.30 ‡	<i>a</i>

* See text.

† Correction made for adsorption of hydroxide by assuming that the total adsorption of hydroxide is the same in the presence of germanium as it is in the blank experiment.

‡ Correction made for adsorption of hydroxide by assuming that the ratio of hydroxide to chloride adsorbed is the same in the presence of germanium as it is in the blank experiment.

(b) When the chloride form of the resin is used, but no other chloride is added :

$$R = (\text{moles of Ge adsorbed}) / (\text{equivs. of Cl in solution at equilibrium})$$

since the germanium must take up the resin sites vacated by the chloride it displaces.

(c) When the resin is washed to the complete removal of germanium and an equivalent amount of the resin is converted into the hydroxide or carbonate form. This can be estimated by passing an excess of 0.5N-sodium chloride solution through the column and determining the alkali liberated in the effluent :

$$R = (\text{moles of Ge adsorbed})/(\text{equivs. of alkali})$$

The third method is tedious, as the complete removal of the germanium is difficult to achieve. However, both the second and the third method have the advantage that it is not necessary to know the capacity of the resin sample used. The results obtained by the three methods are shown in Table 2.

DISCUSSION

The results of the experiments with equimolecular amounts of germanium and chloride [Table 2, (3)] indicate that below pH 9.4 the doubly charged pentagermanate ion ($\text{Ge}_5\text{O}_{11}''$; $R = 2.5$) is the only germanate ion adsorbed by the resin, at least down to pH 6.9. As the pH of the solutions is lowered the amount of pentagermanate adsorbed falls rapidly, its place being taken by chloride ion (Fig. 1). Although this could be caused by a repression of the ionisation of pentagermanic acid, the results of Roth and Schwartz, of Souchay, and of Schwarz and Huf (*loc. cit.*) provide strong evidence that depolymerisation of pentagermanic acid to a monomeric species offers a more likely explanation.

Souchay and Teyssèdre (*loc. cit.*) have pointed out that if Roth and Schwartz's cryoscopic data are interpreted in terms of the presence in germanium dioxide solutions of pentagermanic acid and its ions, then the pH of the solutions should be lower than the values actually found (*ca.* 6). Souchay (*loc. cit.*) attributes the slight acidity of the solutions to an equilibrium, $5\text{H}_2\text{GeO}_3 \rightleftharpoons \text{Ge}_5\text{O}_{11}'' + \text{H}_2\text{O} + 2\text{H}^+$, which is displaced well to the left. Any rise in pH will, however, increase the concentration of pentagermanate ions.

If, as Souchay implies, the monomeric species is a monogermanic acid, it must be a weak acid similar to, if not identical with, that present in solutions of high pH. The steady decrease in the values of R in the range of pH 8.68—4.24 with the minimum amount of chloride present [Table 2, (1)] indicates a progressive replacement of pentagermanate ions by less complex ions (*e.g.*, HGeO_3' , $R = 1$; cf. $\text{HGe}_5\text{O}_{11}'$ for which $R = 5$) as the species adsorbed. However, we prefer not to base any quantitative conclusions on the results obtained with the hydroxide form of the resin in view of the fact that it certainly contained an unknown amount of carbonate which could not be taken into account when calculating the values of R . For example, the value found at pH 4.24, which would suggest the adsorption of a doubly ionised monogermanate ion ($R = 0.5$), seems unlikely, and a value of unity, as suggested above, might have been expected. Nevertheless, the values of R found at pH 7.71 at the intermediate chloride concentrations [Table 2, (2)], which are significantly below the value of 2.5, also provide support for the view that less complex ions are being adsorbed. Such ions cannot be so strongly adsorbed as the pentagermanate or chloride ions, however, as the last two are the only ones adsorbed at higher chloride-ion concentrations [Table 2, (3)].

The steady decrease in the values of R found at pH values above 9.4 (Table 2) shows that the adsorption of pentagermanate ions is giving way to the adsorption of less complex ions. They are apparently less readily adsorbed, for the initial stages of this replacement are accompanied by an increased adsorption of chloride (Fig. 1). The values are compatible with the view that replacement of $\text{Ge}_5\text{O}_{11}''$ by HGeO_3' or by $[\text{Ge}(\text{OH})_5(\text{OH}_2)]'$ occurs first ($R = 1$) and then, at about pH 11, replacement of these by GeO_3'' or $[\text{Ge}(\text{OH})_6]''$ ions takes place ($R = 0.5$). The changes in the slopes of the curves of chloride and germanium adsorption (Fig. 1) at this pH also indicate the adsorption of a more strongly adsorbed ion.

If intermediate polymeric ions such as $\text{Ge}_4\text{O}_9''$ ($R = 2$), $\text{HGe}_2\text{O}_5'$ ($R = 2$), and $\text{Ge}_2\text{O}_5''$ ($R = 1$) are formed as intermediate products of the depolymerisation process, it is evident from Table 2 that they can be adsorbed only over a short pH range, if at all. In fact, although salts such as $\text{M}_2\text{Ge}_4\text{O}_9$ and $\text{M}_2\text{Ge}_2\text{O}_5$ have been found in the systems $\text{Na}_2\text{O}-\text{GeO}_2$

and K_2O-GeO_2 (Schwarz and Heinrich, *Z. anorg. Chem.*, 1932, **205**, 43), no evidence seems yet to have been found for their existence in solution.

The ion-exchange data are consistent with the polymerisation of a monomeric species, possibly a monogermanic acid, to a pentagermanic acid, followed by a depolymerisation to a monogermanic acid again as the pH is raised. Although our data do not permit a distinction between the monogermanic acids formed at high and low pH values, yet Schwarz and Huf's molecular weight determinations (*loc. cit.*) suggest that they are not the same. The pentagermanate ion is evidently not too large to penetrate the resin pores, and the method we have employed should be suitable for studying other small polymeric ions and is in some ways complementary to that of Gustavson and Holm (*Svensk Kem. Tidskr.*, 1952, **64**, 137; cf. also Lister and Macdonald, *J.*, 1952, 4315).

The hydrolysis of the germanate form of the anion-exchanger suggests that the anion of a weak acid is adsorbed. At the same time it contrasts sharply with the strong adsorption of the pentagermanate ion in the presence of a five-fold greater concentration of chloride ion (*i.e.*, when the germanium and chloride concentrations are equal) at pH 9. A likely explanation would appear to be that, as the resin is brought from an alkaline medium to one of distilled water, the pentagermanate ion is hydrolysed to a monomeric form derived from the weaker monogermanic acid (cf. Carpeni, *loc. cit.*; $H_2Ge_5O_{11}$, $pK_1 = 6.2$; H_2GeO_3 , $pK_1 = 9.1$). The weaker acid would then be readily removed from the resin by hydrolysis.

In the experiment where the resin, with both germanium and chloride adsorbed, was left in contact with a limited quantity of water, the amount of germanium left on the resin at equilibrium (Table I) was close to that found to be adsorbed from a germanate solution of the same pH as the aqueous phase (Fig. 1). As this was on the alkaline side of the neutral point it is likely that some alkaline solution was entrained in the resin and that at a slightly lower pH the hydrolysis would have proceeded further.

It is apparent that there is little tendency for the germanate ions present to form complexes with chloride in solutions of the concentrations studied, and no evidence was found of the adsorption of any such complex ions.

The authors thank the Chemical Society and Imperial Chemical Industries Limited for grants.