434. *The Chemistry of Quadrivalent Germanium. Part VI.*[1] *Ion-exchange Studies of More Concentrated Germanate Solutions.*

By D. A. EVEREST and J. C. HARRISON.

Ion-exchange studies of more concentrated germanate solutions have indicated the existence of a heptacondensed germanate ion $H_2Ge_7O_{16}{}^{2-}$. From experiments with resins of different water regain and with near-saturated germanate solutions it is postulated that the equilibrium mono-germanate $\rightleftharpoons$ pentagermanate $\rightleftharpoons$ heptagermanate exists in germanate solutions. This equilibrium is displaced to the right on increasing the germanium concentration and to the left by increasing the pH above pH 9.

IN previous Parts [1-4] the condensation of germanic acid has been studied by ion-exchange techniques, whilst similar methods have been used for studying condensation reactions of boric,[5] arsenious,[6] telluric,[7] and vanadic acids.[8] With germanate solutions, penta-germanate ions $Ge_5O_{11}{}^{2-}$ were taken up by the resin at pH 9, whilst at higher pH values increasing quantities of monogermanate ions were sorbed by the exchanger owing to decondensation of the pentagermanate. Below pH 9 the amount of germanium sorbed by the resin decreased rapidly, although the R value of the sorbed species (*i.e.*, the average number of germanium atoms per " active site " of resin [2,6,8]) tended to remain near 2·5, the required value if the germanium was taken up as pentagermanate. Until recently the existence of pentagermanate in solution appeared to be confirmed both by the above experiments and by the results of other workers using a range of techniques.[9-13] However, Wittman and Nowotny [14] have shown that the solids previously considered to be pentagermanates [15,16] are actually derived from the heptacondensed acid $H_4Ge_7O_{16}$, the general formulæ of these compounds being $M_3HGe_7O_{16}$. Wittman and Nowotny consider that there is no evidence that the pentagermanate ion ever occurs in the solid state, and they also suggest that it is the $HGe_7O_{16}{}^{3-}$ ion which is the condensed germanate species occurring in the vicinity of pH 9 rather than the pentagermanate ion. Similar views have

[1] Part V, Everest and Harrison, *J.*, 1957, 4319.
[2] Everest and Salmon, *J.*, 1954, 2438.
[3] *Idem, J.*, 1955, 1444.
[4] Everest, *J.*, 1955, 4415.
[5] Everest and Popiel, *J.*, 1956, 3183.
[6] *Idem, J.*, 1957, 2433.
[7] *Idem, J. Inorg. Nuclear Chem.*, 1958, **6**, 153.
[8] Russell and Salmon, *J.*, 1958, 4708.
[9] Carpeni and Tchakarian, *Compt. rend.*, 1948, **226**, 725.
[10] Carpeni, *Bull. Soc. chim. France*, 1948, 629.
[11] Schwarz and Huf, *Z. anorg. Chem.*, 1931, **203**, 188.
[12] Souchay and Teyssedre, *Bull. Soc. chim. France*, 1951, 938; Bye, *ibid.*, 1953, 390; Souchay, *ibid.*, 1953, 395.
[13] Lourijsen-Teyssedre, *ibid.*, 1955, 1118.
[14] Wittman and Nowotny, *Monatsh.*, 1956, **87**, 654.
[15] Tchakarian and Carpeni, *Compt. rend.*, 1948, **226**, 1094.
[16] Tchakarian and Wallace, *Bull. Soc. chim. France*, 1954, 1067.

been advanced by Edwards and his co-workers.[17] It is relevant that the compound previously considered to be crystalline pentagermanic acid [18] has been shown to be simply hydrated germanium dioxide.[19]

Re-examination of our ion-exchange data [1,3,4] indicates that R values obtained with germanate solutions up to *ca.* pH 9 are slightly, but significantly, above 2·5, increasing with increasing germanium concentration. As increasing its concentration usually increases the tendency for an acidic species to condense (*e.g.*, refs. 5, 6, and 7), it was considered that by increasing the germanium concentration it might be possible to detect the presence of more highly condensed species than pentagermanate by ion-exchange methods. Experiments have also been carried out on resins of different water regains in order to differentiate between germanate species with different degrees of condensation. This technique has been used by Russell and Salmon for studying the condensation of vanadic acid.[8]

EXPERIMENTAL

Solutions.—Weighed amounts of germanium dioxide were added to 75 ml. of boiled-out distilled water (40 ml. with the experiments with resins of different water regains), the resulting suspension boiled, and the minimum quantity of sodium hydroxide added very slowly to effect solution. After cooling, the pH was adjusted to the required value by addition of alkali. No chloride was present in the solutions used except that added as resin chloride. To prepare the solution containing 870 mg.-atoms of germanium per l., finely-ground germanium dioxide (10 g.) was added to 100 ml. of distilled water. The suspension was heated to 100° for 2—3 hr. with slow addition of 3N-sodium hydroxide (10 ml.), whereupon an optically clear solution was obtained. The pH of the resulting solution was 5·8.

Resins.—Amberlite I.R.A. 400 resin was used in most experiments; its water regain [20] in the chloride form was 0·82 g./g. of resin. The series of resins of different water regains were of the De-Acidite FF type. Their chloride capacities (in mequiv./g. of air-dried form) were respectively 3·91 for the resin of water regain (w.r.) 0·49, 3·12 for w.r. 0·60, 3·40 for w.r. 0·76, 2·85 for w.r. 0·91, 2·17 for w.r. 1·04, and 3·60 for w.r. 2·33.

Equilibrium Experiments.—Solutions were equilibrated with resin (0·25 or 0·5 g. of chloride form) for 14 days with frequent shaking. With resins of low water regain longer was allowed. In experiments with Amberlite I.R.A. 400 the germanium and chloride sorbed by the resin were eluted with 0·5N-sodium hydroxide (100 ml.), then 0·5N-sulphuric acid. Germanium and chloride were determined in aliquot parts of the combined eluate by iodometric [21] and gravimetric procedures respectively. In the experiments with the resins of different water regain the germanium and chloride on the resin at equilibrium were determined indirectly by analysis of the solution phase.

RESULTS AND DISCUSSION

In Fig. 1 are shown R values for the germanate species sorbed on Amberlite I.R.A. 400(Cl) at pH 9 from solutions of different germanium concentrations. This pH was chosen as it is approximately that at which the maximum germanium sorption by the resin occurs.[1-4] The R values obtained increase with increasing germanium concentration, reaching a limiting value of 3·5 which can be accounted for by assuming that germanium is exclusively sorbed as the hepta-condensed species $H_2Ge_7O_{16}{}^{2-}$ from the more concentrated germanate solutions. This ion is similar to the hepta-condensed ion postulated by Wittman and Nowotny [14] and by Shaw *et al.*[17] The R values obtained previously at pH 9 from solutions containing 22·6 and 27·6 mg.-atoms of Ge/l., *i.e.*, 2·6 and 2·8 (interpolated values),[1,4] are in excellent agreement with the R values of 2·6 and 2·75 now obtained at corresponding germanium concentrations.

[17] Shaw, Corwin, and Edwards, *J. Amer. Chem. Soc.*, 1958, **80**, 1536.
[18] Carpeni, *J. Chim. phys.*, 1948, **45**, 130.
[19] Braur and Renner, *Z. anorg. Chem.*, 1955, **278**, 108.
[20] Pepper, Hale, and Reichenberg, *J.*, 1952, 3129.
[21] Everest, *J.*, 1953, 4117.

The results in Fig. 1 might be interpreted as indicating sorption of a mixture of hepta- and mono-germanate ions by the resin, the proportion of the germanium sorbed as hepta-germanate increasing with increasing germanium concentration in solution. This interpretation implies that no pentagermanate ions occur in germanate solution, and that all work indicating the pentagermanate ion [1-4, 9-13] was only a measure of an apparent penta-condensation resulting from a fortuitous ratio of mono- to hepta-germanic acids. It is significant that the concentrations of germanium in the solutions used in these previous investigations were all close to that necessary for the sorption of a germanate of overall R 2·5 by the resin at pH 9 (cf. Fig. 1). However, as discussed below, the above interpretation is not thought to be correct and it is considered that the R values of below 3·5 are due to
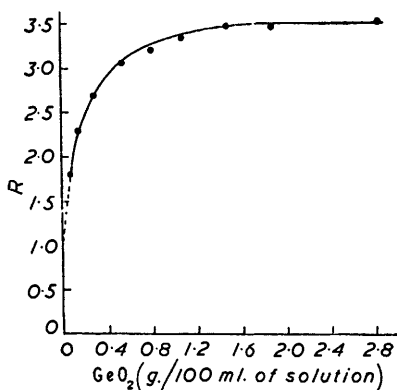

Fig. 1. *Variation of R with germanium concentration at* pH 9 *on Amberlite I.R.A.* 400 *resin.*

the sorption of a mixture of hepta-, penta-, and possibly mono-germanate ions by the resin.

In Fig. 2 are shown R values for the germanate species sorbed by resins of different water regains from a solution containing 132 mg.-atoms of germaniun per l. at pH 9. With resins of water regain 0·60 g./g. and above the R values all approach 3·5, indicating that heptagermanate is the chief germanate species present on these resins at equilibrium. The curve for the actual quantity of germanium sorbed by the 0·60 g./g. resin (Fig. 3) closely follows the R value curve for the resin germanate. It appears that in approaching equilibrium less highly condensed germanate species are initially sorbed by the resin and that these species are subsequently replaced by heptagermanate. All previous work indicates that the concentration of monogermanate is low in a germanate solution of pH 9, especially at the high germanium concentration used in these experiments; it is thus unlikely that monogermanate is the germanium species initially taken up by the exchanger.

With the resin of water regain 0·49 g./g., R remains close to 2·5, even after prolonged contact times, indicating that pentagermanate was the chief germanate species sorbed. With this resin the pore size is too small to allow take up of heptagermanate but it is sufficiently large to allow sorption of pentagermanate, *i.e.*, an ion-sieve effect occurs. This resin also differs in its behaviour from those of higher water regain in that the actual quantity of germanium sorbed by the exchanger slowly increases over a period of *ca.* 28 days whilst the R value of the resin germanate remains constant at 2·5 (Fig. 1). These results indicate both that the pentagermanate is only slowly taken up by the resin and also that no appreciable replacement of the species initially sorbed takes place as the system approaches equilibrium.

At equilibrium the 0·49 g./g. resin has only *ca.* 40% of its capacity occupied by sorbed germanium and only *ca.* 40% of the germanium initially present in solution is actually taken up by the resin. These two quantities are considerably greater in corresponding

experiments with more porous resins. This relatively low equilibrium uptake of germanium could be due to the presence of only a small concentration of pentagermanate in solution, although it would be expected that the selective sorption of pentagermanate by this resin would result in the solution equilibria's being displaced in favour of this ion with a resulting heavy uptake of pentagermanate by the resin. A more plausible explanation

Fig. 2. *Variation of R with time using resins of different water regains. Germanium concentration in solution 132 mg.-atoms/l., pH 9.*

Water regain of resins: *A* 0·49, *B* 0·60, *C* 0·76, *D* 0·91, *E* 1·04, *F* 2·53.
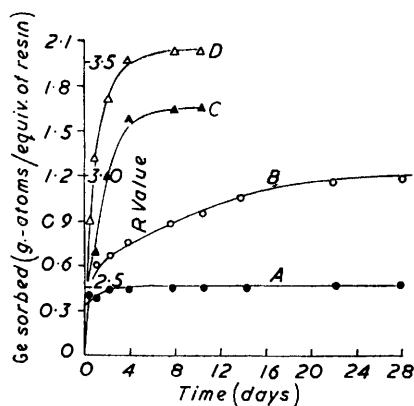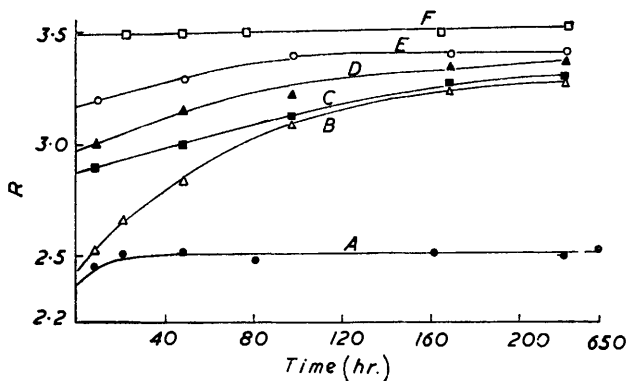

Fig. 3. *Variation with time of the R values and of the quantity of germanium sorbed by resins of water regain 0·49 and 0·60 g./g. Germanium concentration in solution 132 mg.-atoms/l., pH 9.*

A, R values on 0·49 w.r. resin.
B, Ge sorbed on 0·49 w.r. resin, g.-atoms per equiv. of resin.
C, R value on 0·60 w.r. resin.
D, Ge sorbed on 0·60 w.r. resin, g.-atoms per equiv. of resin.

is that pentagermanate is itself partially excluded by the resin owing to variations in the pore size of the latter, this effect being enhanced by the fact that the hepta- and pentagermanate ions cannot differ greatly in size.

The 0·49 g./g. water regain resin was somewhat unstable to alkali. After two treatments with 2N-sodium hydroxide its water regain had risen to 0·55 and the resin was no longer excluding heptagermanate. It appears that when resins of known water regain are used as ion-sieves the water regain should be checked after each loading–elution cycle.

It is suggested from both present and previous results that the following equilibria exist in germanate solutions:

$$\text{Monogermanate} \rightleftharpoons \text{pentagermanate} \rightleftharpoons \text{heptagermanate}$$
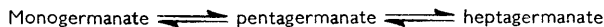
these equilibria being shifted to the right by increasing the germanium concentration and to the left by increasing the pH above pH 9. The solutions investigated by Wittman and Nowotny [14] and by Shaw *et al.*[17] were relatively concentrated and would thus contain principally heptagermanate, but the more dilute solutions used by other workers would contain principally pentagermanate as the most highly condensed germanate species. It appears that in its condensations germanic acid shows many resemblances to boric [5] and telluric acids.[7]

In Fig. 4 are shown R values for germanate sorbed on Amberlite I.R.A. 400 from solutions containing 178·1 mg.-atoms of Ge/l. between pH 5·8 and 10.   With these solutions not only is the $H_2Ge_7O_{16}{}^{2-}$ ion the only germanate species sorbed by the resin below pH 9·7 but, more significantly, only little change occurs in the actual quantities of germanium and chloride sorbed by the resin (3·05 and 0·10 at pH 9·75 and 2·96 and 0·145 at pH 6·5, g.-atoms of Ge and Cl per equiv. of resin respectively).   This exclusive sorption of hepta-germanate and the constant germanium : chloride ratio on the resin is due to two factors. First, the high affinity of the heptagermanate ion for the resin (in absence of the ion-sieve effect) as compared with the resin affinity of the other ionic species present; this greater affinity of the heptagermanate is due to its high polarisability (the relation between the resin affinity and the polarisability of an ion is discussed elsewhere [22]).   Secondly, the high ratio of germanium in solution both to the total chloride in the system and to the amount of germanium sorbed by the resin (0·25 g. of chloride-form resin equilibrated with 75 ml. of germanate solution).

Experiments were also carried out on the sorption of germanium by a high water-regain resin (2·3 g./g.) from the most concentrated germanium solution it was possible to
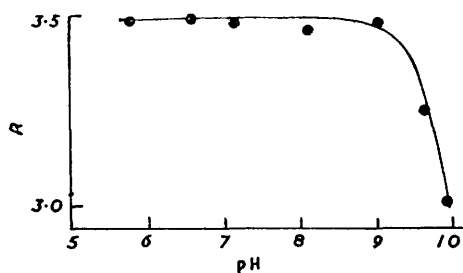

FIG. 4.   *Variation of R with pH of solution on Amberlite I.R.A. 400.   Germanium concentration 178·1 mg.-atoms/l.*

produce (870 mg.-atoms of Ge/l.).   At pH 5·8 equilibrium between the resin and the solution phase was only slowly attained, R for the sorbed germanate being 2·8 after 24 hr., rising to 3·42 after 21 days.   This slow attainment of equilibrium is probably due to the presence of only a small equilibrium concentration of heptagermanate in solution, a slow displace-ment of the solution equilibria taking place in favour of heptagermanate as this ion is removed by the resin from the solution phase.

At pH 8·1 equilibrium was rapidly attained, R reaching 3·5 after 24 hr. and remaining close to this value for 11 days.   These results confirm that heptagermanate is the principal species present in concentrated germanate solutions at *ca.* pH 8—9.   It was also found that affer 21 days R had risen to 4·14.   This result probably indicates that a more highly condensed species than heptagermanate occurs in trace quantities in concentrated germanate solutions, at least in the pH range 8—9.

BATTERSEA COLLEGE OF TECHNOLOGY,
          LONDON, S.W.11.
[Present Address (D. A. E.).—NATIONAL CHEMICAL LABORATORY,
          TEDDINGTON.]   [*Received, January 28th,* 1959.]

[22] Aveston, Everest, and Wells, *J.*, 1958, 231;   Everest, Napier, and Wells, Conference for the Peaceful Uses of Atomic Energy, Geneva, 1958, paper A/Conf. 15/P/101.