133. *The Chemistry of Bivalent Germanium Compounds. Part III.* The Polarographic Behaviour of Bivalent Germanium.*

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The reduction and oxidation of bivalent germanium at the dropping-mercury electrode have been studied in hydrochloric and in hypophosphorous acid solution. The behaviour observed supported the postulate that the electrode reaction involved the Ge^{++} ion although bivalent germanium probably entered into complex formation with both solvents.

A CATHODIC wave, due to the reduction Ge(II) ⟶ Ge, has been found in 6N-hydrochloric acid by Alimarin and Ivanov-Emin (*J. Gen. Chem., U.S.S.R.*, 1944, **17**, 204). The half-wave potential ($E_{\frac{1}{2}}$) was approximately —0·5 v in 6N-hydrochloric acid (relatively to the mercury pool anode), $E_{\frac{1}{2}}$ moving to more positive values on increase in the germanium concentration or on decrease of that of the hydrochloric acid. An anodic wave, due to the oxidation Ge(II) ⟶ Ge(IV), has been observed by Cozzi and Vivarelli (*Mikrochem. Mikrochim. Acta*, 1951, **36**/**37**, 594), who found that this wave was obscured by that due to the chloride ion if the concentration of the latter exceeded 2N; this interference was reduced on addition of cadmium sulphate, which removed some of the chloride ions by formation of complexes such as $CdCl_4^{=}$.

The present investigation has been carried out in two solvents, hydrochloric and hypophosphorous acids, and the results will be considered under these two headings.

Effect of concentrations of germanium and of acid.

Hydrochloric acid solutions.

	3·1N-HCl		Ge concn., 2·43 × 10^{-3}M			
Ge concn., 10^{-3}M	$E_{\frac{1}{2}}$, anodic	$E_{\frac{1}{2}}$, cathodic	Acid, N	$E_{\frac{1}{2}}$, anodic	$E_{\frac{1}{2}}$, cathodic	D.C.C.
2·39	—	−0·49	3·54	—	−0·51	3·21
3·23	—	−0·49	2·82	—	−0·475	3·30
3·31	—	−0·49	2·74	—	−0·46	3·21
3·58	—	−0·485	1·63	—	−0·43	2·38
4·96	—	−0·48	1·09	—	−0·42	2·20
6·89	—	−0·47	0·55	—	−0·42	1·47

Hypophosphorous acid solutions.

	3·9N-H_3PO_2		Ge concn., 2·09 × 10^{-3}M			
1·21	−0·175	−0·57	3·82	−0·17	−0·565	—
2·36	−0·17	−0·565	3·11	−0·175	−0·565	—
3·37	−0·175	−0·575	2·64	−0·185	−0·55	—
4·47	−0·17	−0·57	1·67	−0·185	−0·55	—
4·81	−0·17	−0·575	1·19	−0·19	−0·54	—
6·11	−0·17	−0·57	0·96	−0·19	−0·53	—

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EXPERIMENTAL

Apparatus.—A photographically recording Cambridge polarograph was used for the main part of this work; measurements, except where otherwise stated, were made relative to the saturated calomel electrode (S.C.E.). The $m^{2/3}t^{1/6}$ factors for the capillaries were measured in 0·1N-potassium chloride on open circuit and had values of 1·021, 1·470, 1·669, and 2·699 (see p. 662).

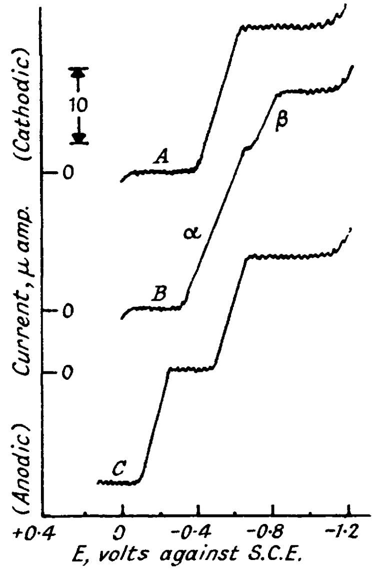
Procedure.—For the experiments in hydrochloric acid, germanium dioxide (0·1—0·2 g.) was accurately weighed and reduced to the bivalent state by heating it to 100° for 1 hour with 3N-hydrochloric acid (32·5 ml.) and 50% hypophosphorous acid (2·5 ml.); 25% hypophosphorous acid (35 ml.) was used for the reduction in the chloride-free experiments. These were used as stock solutions, known volumes of which were accurately diluted to the required concentration.

It was not found necessary to deoxygenate the solutions used, their strongly reducing character removing any dissolved oxygen present, and any loss of bivalent germanium thereby incurred being negligible at the concentrations used (1—9 × 10^{-3}M). If the polarographic runs were carried out rapidly, an inert atmosphere was not found essential, bivalent germanium being fairly stable in air, especially in presence of hypophosphorous acid. The reliability of this procedure was shown by the constancy of the diffusion current constant (D.C.C.) values obtained from different experiments. All runs were carried out at 25°.

Wave *A*. Ge *concn.*, 3·58 × 10^{-3}M; $m^{2/3}t^{1/6}$ = 1·669; *solvent*, 3·1N-HCl.

Wave *B*. Ge *concn.*, 8·26 × 10^{-3}M; $m^{2/3}t^{1/6}$ = 1·021; *solvent*, 4·3N-HCl.

Wave *C*. Ge *concn.*, 4·47 × 10^{-3}M; $m^{2/3}t^{1/6}$ = 1·669; *solvent*, 3·9N-H_3PO_2.



Results.—*Hydrochloric acid.* Well-defined cathodic waves were obtained (Wave *A*, Fig.), exhibiting maxima which could be suppressed by addition of 0·005—0·008% of methyl cellulose which had no effect upon the magnitude of the diffusion current. It was found, in agreement with Alimarin and Ivanov-Emin (*loc. cit.*), that $E_{\frac{1}{2}}$ moved to more positive values on decrease of hydrochloric acid concentration or on increase of that of the germanium (see Table). If a mercury pool anode was used (cf. *idem, ibid.*) the $E_{\frac{1}{2}}$ values were more positive than when measured against the S.C.E. (*e.g.*, −0·33 v in 4·3N-hydrochloric acid as against the S.C.E. value of −0·47 v in 3·1N-hydrochloric acid; germanium concentration 6·8 × 10^{-3}M); the mercury anode had a potential of about −0·15 to −0·2 v against the S.C.E. Similar behaviour was found by Smyz (*Rec. Trav. chim.*, 1925, **44**, 580) in the electrolysis of stannous salts, the mercury anode acquiring a potential of about −0·15 v against the S.C.E. The decrease in the D.C.C. with decreasing acid concentration (see Table) was probably due to hydrolysis which reduced the effective germanium concentration. As reported by Alimarin and Ivanov-Emin (*loc. cit.*), metallic germanium was the reduction product in both hydrochloric and hypophosphorous acids, *i.e.*, *n* (the number of electrons in the reduction) = 2.

When the germanium concentration was increased above a certain value, depending upon the $m^{\frac{2}{3}}t^{\frac{1}{6}}$ factor, the cathodic wave split into two parts (α and β, wave B); the first wave (α) had a constant height, but the second (β) increased with increasing germanium concentration. The germanium concentrations at which splitting occurred were: 6·20, 10·1, and 14·0 × 10^{-3}M in 4·3N-hydrochloric acid, and 9·1 × 10^{-3}M in 3·1N-hydrochloric acid, the corresponding $m^{\frac{2}{3}}t^{\frac{1}{6}}$ factors being 1·021, 1·470, 2·699, and 1·669. The overall D.C.C. for the double wave ($\alpha + \beta$) was 3·42 ± 0·02 as compared with 3·22 ± 0·02 for the ordinary single wave obtained below the splitting concentration (*e.g.*, wave *A*, Fig.), thus making $n = 2{\cdot}13$ for the overall double-wave. This value was sufficiently near to 2 to show that the double wave ($\alpha + \beta$) was due only to reduction to elementary germanium, and that no new reduction products were formed. This behaviour was similar to that observed by Lingane and Niedrach in the polarographic reduction of quadrivalent selenium and tellurium (*J. Amer. Chem. Soc.*, 1949, **71**, 196). A probable explanation, based on that advanced by these authors, was that the constancy of the first wave height was due to the formation of a film of elementary germanium on the surface of the mercury drop, and that this interfered with the electrode reaction, causing further deposition to occur at more negative potentials.

The anodic wave observed by Cozzi and Vivarelli (*loc. cit.*) has been confirmed; it has been studied chiefly in hypophosphorous acid solution because the chloride of the hydrochloric acid caused interference.

Hypophosphorous acid. With this acid as solvent (total acid maintained at 3·5N, germanium concentration 2·4 × 10^{-3}M) the values of $E_{\frac{1}{2}}$ (cathodic) moved to more negative values (−0·51 to −0·565) whilst the D.C.C. changed from 3·22 ± 0·02 to 2·03 ± 0·04. Both the anodic and the cathodic waves were well defined in hypophosphorous acid (Wave C, Fig.), the D.C.C. for the anodic wave being −2·01 ± 0·03. The effects of the concentrations of germanium and of hypophosphorous acid on the $E_{\frac{1}{2}}$ values are shown in the Table, these two factors having no effect on the magnitude of either D.C.C. values. As in hydrochloric acid, the cathodic waves split into two parts above a certain germanium concentration. The behaviour of these split waves was similar to that shown in hydrochloric acid.

Discussion

Hydrochloric Acid.—The positive shift of $E_{\frac{1}{2}}$ (cathodic) with decreased hydrochloric acid concentration (see Table) was consistent with reduction involving the Ge^{++} ion, the concentration of which would decrease with increased chloride concentration owing to the formation of ions such as $GeCl_3^-$. Analogous behaviour has been found by Riccoboni, Popoff, and Arich (*Gazzetta*, 1949, **79**, 547) in the polarographic reduction of stannous salts, $E_{\frac{1}{2}}$ decreasing from —0·54 to —0·45 v on decrease of the chloride concentration from 4·0 to 0·1M. These authors considered that it was the Sn^{++} ion which was reduced, the concentration of which would be similarly decreased with increasing chloride concentration owing to formation of chloro-complexes.

Hypophosphorous Acid.—The cathodic reaction in hypophosphorous acid also presumably involved the simple Ge^{++} ion. The more negative values of $E_{\frac{1}{2}}$ (cathodic) in hypophosphorous compared with hydrochloric acid, at any given germanium and acid concentration, probably indicated complex formation between bivalent germanium and hypophosphorous acid. This hypothesis was supported by the negative shift of $E_{\frac{1}{2}}$ (anodic) and positive shift of $E_{\frac{1}{2}}$ (cathodic) with decreasing hypophosphorous acid concentration (see Table). Insufficient is known, however, about complexes involving hypophosphorous acid for any definite conclusions to be drawn. The similarly of the D.C.C. values for the anodic and cathodic waves (—2·01 ± 0·03 and 2·03 ± 0·04) indicated that the same entities were involved in both anodic and cathodic processes.

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