CCLX.—*Germanium. Part V. The Hydrolysis of Sodium Germanate and the Dissociation Constants of Germanic Acid.*

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THE preparation of various salts of germanic acid, including sodium germanate, has already been described by the author (J., 1926, 2828), and in another communication (this vol., p. 1537) it has been shown that germanium dioxide in aqueous solution is essentially an acid. It was hoped that the solubility determinations of the latter investigation could be employed in the calculation of the acid and the basic dissociation constants of germanic acid, but as they did not admit of such treatment, the present investigation was undertaken.

In aqueous solutions of sodium germanate the following equilibria are set up :

$$Na_2GeO_3 \rightleftharpoons 2Na^{\cdot} + GeO_3'';$$
$$HOH \rightleftharpoons OH' + H^{\cdot},\ [H^{\cdot}][OH'] = K_w;$$
$$HGeO_3' \rightleftharpoons H^{\cdot} + GeO_3'',\ [H^{\cdot}][GeO_3'']/[HGeO_3'] = K_2;$$
$$H_2GeO_3 \rightleftharpoons H^{\cdot} + HGeO_3',\ [H^{\cdot}][HGeO_3']/[H_2GeO_3] = K_1;$$
$$H_2GeO_3 \rightleftharpoons 2H^{\cdot} + GeO_3'',\ [H^{\cdot}]^2[GeO_3'']/[H_2GeO_3] = K_1K_2$$
$$H_2O + GeO_3'' \rightleftharpoons OH' + HGeO_3',\ [OH'][HGeO_3']/[GeO_3''] = K_h = K_w/K_2.$$

Of the above constants, apart from K_w, only one, K_1, has hitherto been determined, Roth and Schwartz (*Ber.*, 1926, **59**, 338) having obtained the value $1{\cdot}2 \times 10^{-7}$ by measuring the conductivity of aqueous solutions of germanium dioxide. Electrometric titrations of sodium germanate solutions, described later, show that the salt $NaHGeO_3$ exists in solution, and it is therefore reasonable to calculate the degree of hydrolysis according to the hydrolytic equilibrium $Na_2GeO_3 + H_2O \rightleftharpoons NaHGeO_3 + NaOH$. The sodium hydroxide produced is largely ionised in solution, but it can only be regarded as completely ionised in dilute solution or when the degree of hydrolysis is small, and hence the measurement of the hydroxyl-ion concentration does not give a true measure of hydrolysis. This can only be given by the total concentration of sodium hydroxide, dissociated and undissociated. Some investigators, in similar cases, take as the concentration of sodium hydroxide that which would give the same hydroxyl-ion concentration in a pure solution of sodium hydroxide. With the dilute solutions employed here, such corrections were considered inadvisable, the more especially because the equally important correction for the influence of the unhydrolysed sodium salts on the ionisation of sodium hydroxide is unknown. In the calculation of the degree of hydrolysis, therefore, it is assumed that the sodium hydroxide is completely ionised; the small error thus introduced diminishes with the concentration of the solutions employed.

Preparation of Material.—Pure germanium dioxide was fused to a homogeneous melt in a nickel crucible with about 10% more than the theoretical amount of sodium hydroxide required for the formation of metagermanate. The cooled melt was extracted with the minimum quantity of boiling water, and any insoluble matter was filtered while the liquid was still hot. The clear solution was then evaporated over concentrated sulphuric acid and seeded from time to time with crystals of the heptahydrate, $Na_2GeO_3,7H_2O$. Clear, transparent crystals were deposited in the course of a few days, and were well washed with small quantities of ice-cold water. Analysis having shown that they contained a very small excess of alkali, they were recrystallised. This was best done from very dilute solutions of caustic soda : in the absence of a small excess of free alkali, concentrated solutions of sodium germanate deposit minute traces of flocculent germanium dioxide on standing for several days. One recrystallisation was sufficient to give a very pure product. If the crystals so obtained were allowed to dry they did not redissolve to a clear solution; a small residue, presumably of hydrated germanium dioxide, always remained. The presence of carbon dioxide in the water had to be excluded for the same reason. This separation of solid matter did not, however, occur when the crystals were dissolved, while still moist, in recently boiled water. This precaution was taken throughout.

EXPERIMENTAL.

Measurement of Hydrolysis.—Of the many methods available for the determination of the degree of hydrolysis, the best and most accurate is undoubtedly the measurement of the hydrogen-ion concentration by means of the hydrogen electrode. Throughout this work the *E.M.F.* was measured of the following combination :

$$\mathrm{Pt,H_2}\left|\mathrm{Na_2GeO_3}\right\|\mathrm{KCl(satd.)}\left\|\begin{matrix}\mathrm{KCl(satd.)}\\ \mathrm{Hg_2Cl_2}\end{matrix}\right|\mathrm{Hg.}$$

Preliminary experiments showed that suitable electrodes attained equilibrium rapidly and gave consistent results. Sheet platinum electrodes prepared in the usual way became sluggish in the course of a few hours. On the other hand, the film electrodes on glass finally adopted were much more active : they attained equilibrium rapidly and maintained their activity for 6—8 hours. When they showed signs of sluggishness they were heated, "refilmed," and "reblacked," and were then found to be quite as efficient as before. The hydrogen half-element employed was the usual laboratory type suggested by Sörensen. The hydrogen was prepared from pure zinc and sulphuric acid, to which a few drops of copper sulphate solution had been added, and was purified by the method recommended by Clark (" Determination of Hydrogen Ions ").

The calomel half-element was of the saturated type, prepared with great care. It was checked with a normal calomel electrode and with certain standard buffer solutions, and its potential, referred to the normal hydrogen electrode, was 0·2500 volt.

The *E.M.F.* measurements were made on a Tinsley potentiometer, the current being supplied by an accumulator which was balanced just before and after each reading against a standard Weston cell. The point of balance was determined by means of a very sensitive reflecting galvanometer. All measurements were made at 20°.

The two half-elements were joined in all cases through a saturated solution of potassium chloride which was considered to eliminate completely the liquid–liquid potential difference. This view is not strictly correct, but the error introduced is almost certainly not greater than 0·1 millivolt with the dilute solutions used, as judged from Harman's results for the hydrolysis of the analogous sodium silicates (*J. Physical Chem.*, 1926, **30**, 1100), in which, for *N*/10-solutions, the liquid–liquid potential differences as determined experimentally and as calculated by the Henderson formula are 0·0 and 0·1 millivolt, respectively.

From the observed *E.M.F.* the hydrogen-ion concentration was calculated by means of the relation

$$p_{\mathrm{H}} = [E.M.F.(\text{obs.}) + E.M.F.(\text{bar.}) - E.M.F.(\text{calomel})]/0{\cdot}05812,$$

and from the values of the hydrogen-ion concentration, so found, the values of the hydroxyl-ion concentration have been calculated from the dissociation constant of water, K_w being taken as $1{\cdot}0 \times 10^{-14}$.

The results are given in Table I and shown graphically in Fig. 1, where percentage hydrolysis is plotted against concentration. Obviously, sodium germanate is very largely hydrolysed in solution. For the purposes of comparison, the degrees of hydrolysis in *N*/10-solutions of sodium silicate (Harman, *loc. cit.*) and sodium carbonate are appended below. The value for sodium carbonate has been calculated from one of the results obtained by Frary and Nietz (*J. Amer. Chem. Soc.*, 1915, **37**, 2268).

Na_2CO_3.	Na_2SiO_3.	Na_2GeO_3.
0·096	0·414	0·615

This increase in hydrolysis is just what would be anticipated from the position of the three elements in the same group of the periodic classification. It is to be expected, therefore, that the dissociation constants of germanic acid will be much smaller than those of carbonic acid.

Hydrolysis Constant.—This is given by the relation

$$K = [NaHGeO_3][NaOH]/[Na_2GeO_3],$$

where the concentrations of the different substances include both the ionised and the un-ionised portions. It is obvious that K will vary with the dilution, since it involves the degrees of dissociation of the three compounds, and its value will approach K_h as a limit at infinite dilution.

FIG. 1.

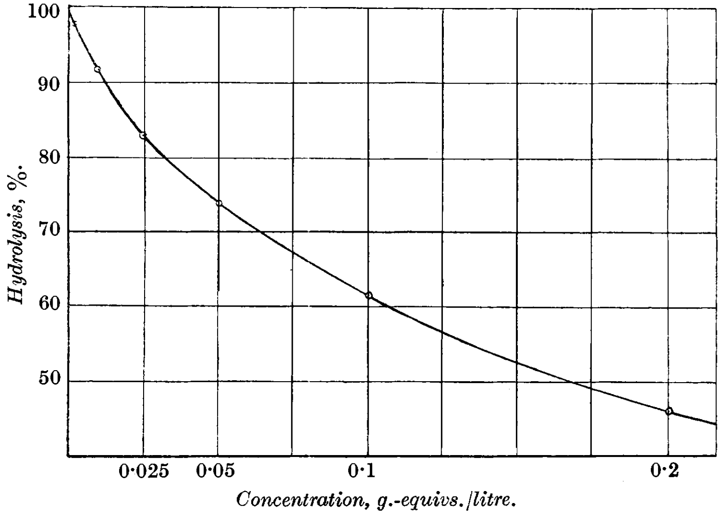


TABLE I.

Na_2GeO_3, mols./l.	*E.M.F.*, corr.	p_H.	$[H^\cdot] \times 10^{12}$.	[OH′].	Hydrolysis, %.
0·100	0·9858	12·66	0·217	0·0461	46·1
0·050	0·9756	12·49	0·325	0·0308	61·5
0·025	0·9627	12·27	0·541	0·0185	74·0
0·0125	0·9482	12·02	0·961	0·0104	83·3
0·005	0·9277	11·66	2·18	0·0046	92·0
0·001	0·8886	10·99	10·2	0·00098	98·0

If, in the equilibrium

$$Na_2GeO_3 + H_2O \rightleftharpoons NaHGeO_3 + NaOH,$$

c represents the concentration of sodium germanate (in mols./l.) and x its degree of hydrolysis, then $K = cx^2/(1 - x)$. The values of K

for the various values of c and x are given in Table II. Too much significance must not be placed on the last value of K, because at that dilution the cell has a big internal resistance and the null point is not so readily found—a very small error in the *E.M.F.* makes a big difference in the value of K. The limiting value, K_h, appears to be about $5{\cdot}4 \times 10^{-2}$.

TABLE II.

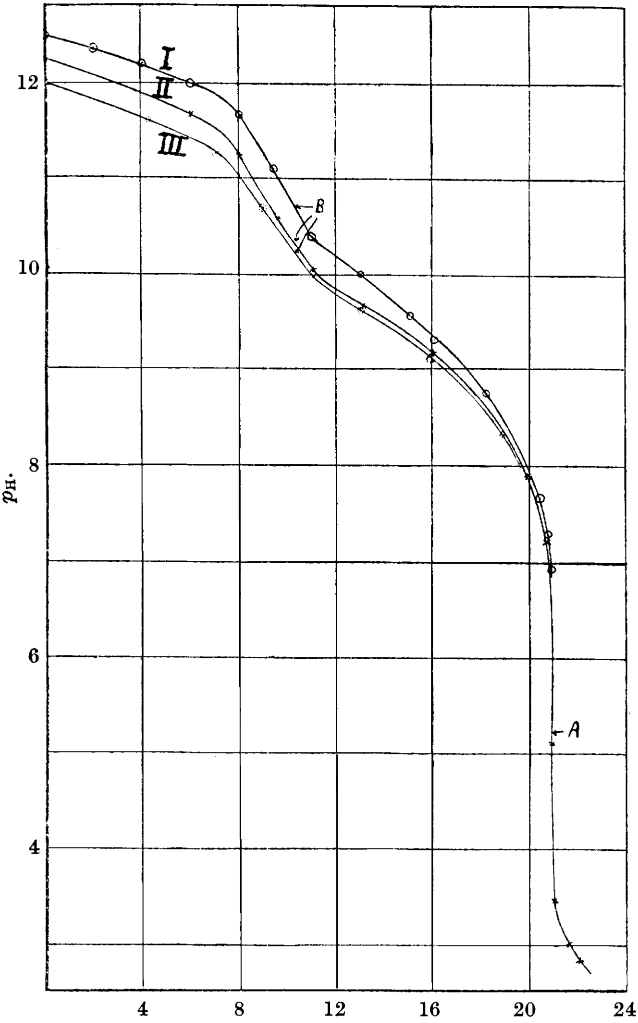
c	0·100	0·050	0·025	0·0125	0·005	0·001
x	0·461	0·615	0·740	0·833	0·920	0·98
K	0·0394	0·0491	0·0526	0·0524	0·053	0·049

The Secondary Dissociation Constant of Germanic Acid.—The value of this constant, K_2, may now be calculated from the hydrolysis constant by means of the relation $K_2 = K_w/K_h = 10^{-14}/5{\cdot}4 \times 10^{-2} = 1{\cdot}9 \times 10^{-13}$.

The value of the secondary dissociation constant of carbonic acid is 6×10^{-11} at 25°. It should be noted that the value of K_2 obtained above is independent of the assumptions made with regard to the ionisation of sodium hydroxide, because the limiting value of the hydrolysis constant has been used for its evaluation.

Electrometric Titrations.—In an earlier paper (*loc. cit.*) the author states that sodium germanate, like sodium carbonate, can be quantitatively titrated with a strong acid in the presence of a suitable indicator. Methyl-orange is suitable for this purpose, but phenolphthalein is quite unsuitable. By carrying out this titration electrometrically it is possible to obtain much information about the behaviour of germanic acid in solution. Three such titrations have been carried out : (1) 0·1N-Na_2GeO_3 with 0·097N-HCl, (2) 0·05N-Na_2GeO_3 with 0·0485N-HCl, (3) 0·025N-Na_2GeO_3 with 0·0242N-HCl. A wide test-tube was used as the electrode vessel, the various connexions being made through a suitably bored, tight-fitting rubber stopper. Hydrogen was allowed to pass through the cell until the *E.M.F.* was constant and then small amounts of hydrochloric acid were added, the *E.M.F.* being allowed to attain its equilibrium value after each addition. The results obtained are shown graphically in Fig. 2, where the p_H value is plotted against the volume of acid added to 20 c.c. of germanate solution. In all three cases there is an unmistakable break in the curve after the addition of about 40% of the total acid required for complete neutralisation, followed by another and more sudden drop from p_H 7·5 to p_H 3. This is clear evidence of the existence of sodium hydrogen germanate in solution, the curves being typical of the neutralisation curves of dibasic acids. Germanic acid, therefore, ionises in two stages as shown on p. 1994. The first break in the curves corresponds to the second-stage ionisation. If the break at the half-neutralisation had been sharper it would have been possible to calculate K_2 from the p_H value at that point. This lack of sharpness is due to hydrolysis of the sodium hydrogen germanate, and the degree of hydrolysis of this salt may now be calculated as follows: At the half-neutralisation point, B, the reaction $Na_2GeO_3 + HCl \longrightarrow NaHGeO_3 + NaCl$ has

FIG. 2.



I. $N/10$-Na_2GeO_3 *with* $N/10$-HCl. II. $N/20$-Na_2GeO_3 *with* $N/20$-HCl.
III. $N/40$-Na_2GeO_3 *with* $N/40$-HCl.

occurred, and the acid salt is now the source of hydroxyl ions, $HGeO_3' + H_2O \rightleftharpoons H_2GeO_3 + OH'$. Assuming complete ionisation, we have for the $0{\cdot}1N$-solution (I in Fig. 2), which is now 0·033 molar: $p_H = 10{\cdot}65$; $[H^{\cdot}] = 2{\cdot}3 \times 10^{-11}$; $[OH'] = 4{\cdot}3 \times 10^{-4}$, and the percentage hydrolysis is $100(4{\cdot}3 \times 10^{-4}/0{\cdot}033) = 1{\cdot}3\%$. For the $0{\cdot}025N$-solution (III in Fig. 2) (now 0·00833 molar) the corresponding value of p_H is 10·25, whence the percentage hydrolysis is 2·2%.

The Primary Dissociation Constant of Germanic Acid.—This constant may be evaluated in two ways : (i) from the hydrolysis data of sodium hydrogen germanate, and (ii) from the p_H value at the point of complete neutralisation, point A on the curve.

K_1 *from hydrolysis data.* For the hydrolysis of sodium hydrogen germanate

$$\begin{aligned} K_h &= [H_2GeO_3][OH']/[HGeO_3'] \\ &= [H_2GeO_3]K_w/[H^{\cdot}][HGeO_3'] = K_w/K_1. \end{aligned}$$

If c and x represent its concentration and degree of hydrolysis, respectively, $K_h = cx^2/(1 - x)$, whence for $c = 0{\cdot}033$, $K_h = 5{\cdot}7 \times 10^{-6}$, $K_1 = 1{\cdot}75 \times 10^{-9}$; and for $c = 0{\cdot}00833$, $K_h = 4{\cdot}0 \times 10^{-6}$, $K_1 = 2{\cdot}5 \times 10^{-9}$; mean $K_1 = 2{\cdot}1 \times 10^{-9}$.

K_1 *from the* p_H *value at the neutral point.* Only one of the solutions, $0{\cdot}05N$, was titrated to a marked degree of acidity. In this case, the middle point A of the large break (see Fig. 2) occurs at $p_H = 5{\cdot}20$, and at this point the amount of hydrochloric acid added corresponds exactly to that required to combine with all the sodium present. The acidity of the solution at this point is therefore due to germanic acid which is now $0{\cdot}025N = 0{\cdot}0125$ molar. Hence

$$p_H = 5{\cdot}20;\ [H^{\cdot}] = [HGeO_3'] = 6{\cdot}3 \times 10^{-6};\ [H_2GeO_3] = 0{\cdot}0125;$$
$$K_1 = (6{\cdot}3 \times 10^{-6})^2/0{\cdot}0125 = 3{\cdot}2 \times 10^{-9}.$$

20 C.c. of sodium germanate solution required, by the electrometric method, 20·70 c.c., and with methyl-orange, 20·75 c.c. of hydrochloric acid for complete neutralisation. The best indicator for the titration is not methyl-orange but one with a colour change at approximately p_H 5, *e.g.*, methyl-red (p_H 4·4—6·0).

The values of the dissociation constants obtained by the different methods are compared below.

	By hydrolysis.	By *E.M.F.*
K_1	$2{\cdot}1 \times 10^{-9}$	$3{\cdot}2 \times 10^{-9}$
K_2	$1{\cdot}9 \times 10^{-13}$	—

The two values for K_1 agree very well and give a mean value of $2{\cdot}6 \times 10^{-9}$. This value is nearly 50 times smaller than that (*viz.*,

$1{\cdot}2 \times 10^{-7}$) obtained by Roth and Schwartz (*loc. cit.*) using the conductivity method at 25°, but the small temperature difference seems insufficient to account for the big difference in the two values. According to Roth and Schwartz, germanic acid is one-third as strong as carbonic acid (3×10^{-7}). This does not seem to be very likely in view of the position of carbon and germanium in the periodic classification, silicon being interpolated between them. Much bigger differences are found between the dissociation constants of the nitrogen acids and the corresponding acids of arsenic (Stieglitz, "Elements of Qualitative Chemical Analysis," p. 104). In the opinion of the author, therefore, the value obtained by Roth and Schwartz is too high and is probably due to the high conductivity of the water employed. In view of the values obtained in this investigation, it is questionable if their argument is a sound one, namely, that the much higher concentration of the weaker germanic acid so effectively represses the ionisation of the carbonic acid that its influence on the conductivity can be neglected. A small trace of carbon dioxide in the solution would in all probability substantially add to its hydrogen-ion concentration.

Summary.

(1) The degree of hydrolysis of sodium germanate in solution has been determined at various concentrations by the hydrogen-electrode method.

(2) The limiting value of the hydrolysis constant is $5{\cdot}4 \times 10^{-2}$.

(3) The secondary dissociation constant of germanic acid, $1{\cdot}9 \times 10^{-13}$, has been calculated from the hydrolysis constant.

(4) Electrometric titrations of sodium germanate have been carried out which show that germanic acid is a dibasic acid.

(5) The primary dissociation constant of germanic acid, $2{\cdot}6 \times 10^{-9}$, is 45 times smaller than the value obtained by Roth and Schwartz. The reasons for the discrepancy are discussed.

In conclusion, the author wishes to thank Professor Newbery for the use of his potentiometer, and to make acknowledgment to Professor J. Smeath Thomas for the loan of the material and for the interest he has shown in the progress of the work.

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