#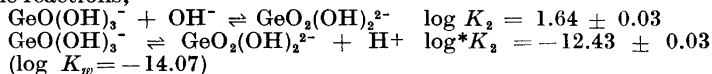 On the Determination of the Formation Constants of GeO$_2$(OH)$_2^{2-}$ Using a Hydrogen-Electrode. Measurements in 3 M Na(Cl)-Medium.

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The formation constant of GeO$_2$(OH)$_2^{2-}$ at 25°C in a 3 M NaCl medium has been determined using a hydrogen electrode. We find for the reactions,

GeO(OH)$_3^-$ + OH$^-$ ⇌ GeO$_2$(OH)$_2^{2-}$ log K_2 = 1.64 ± 0.03
GeO(OH)$_3^-$ ⇌ GeO$_2$(OH)$_2^{2-}$ + H$^+$ log*K_2 = −12.43 ± 0.03
(log K_w = −14.07)

In the range studied there were no indications of the formation of polyanions.

One of us has made an emf investigation [1] on the hydrolysis reactions of germanate ions in 0.5 m (molality) Na(Cl) solution within the range 2 < −log[H$^+$] < 11. The data indicated that, in addition to the mononuclear species, Ge(OH)$_4$, GeO(OH)$_3^-$, GeO$_2$(OH)$_2^{2-}$, there are also considerable amounts of a polynuclear species, which contains eight germanium atoms and has the charge −3. In titrations where hydroxide ions were added to a dilute Ge(OH)$_4$ solution ([Ge]$_{total}$ < 0.010 m), clear solutions were always obtained, but at higher concentrations (*e.g.* 0.030 m) a white precipitate was obtained. This precipitate appeared when the mean charge, Z, of the germanium species in the solution reached the value $Z \approx -0.4$. On adding more alkali the precipitate dissolved and at $Z \approx -1$ the solution became clear again. In most of the titrations the free hydrogen ion concentration was measured with a glass electrode, but in a few titrations a hydrogen electrode was also used. In the range, −log[H$^+$] < 9.5 ($Z \approx -0.6$), the glass and the hydrogen electrodes always agreed within ± 0.2 mV.

The present work was started in order that solutions in which the average negative charge per germanium species is > 1 might also be studied; the aim of the work being to see whether polyanions are still present or not and to get a value for the second dissociation constant of germanic acid.

NOTATION

B total concentration of Ge
E measured emf in millivolts (mV), $E = E_o + 59.155 \log[OH^-] + E_j$
E_o a constant in the expression for E
E_j liquid junction emf, $E_j = \text{const} [OH^-]$
Z average negative charge per germanium = average number of OH^- bound per $Ge(OH)_4$.

The formation of the complex $GeO_2(OH)_2^{2-}$ can be written either with H^+ or OH^- as reactant. We shall denote the corresponding overall constants by $*\beta_2$ and β_2 (formation of $GeO_2(OH)_2^{2-}$ from $Ge(OH)_4$) and the step-wise constants by $*K_2$ and K_2 (formation of $GeO_2(OH)_2^{2-}$ from $GeO(OH)_3^-$). Thus, $[GeO_2(OH)_2^{2-}] = K_2 [GeO(OH)_3^-] [OH^-] = *K_2 [GeO(OH)_3^-] [H^+]^{-1}$ and $[GeO_2(OH)_2^{2-}] = \beta_2 [Ge(OH)_4] [OH^-]^2 = *\beta_2 [Ge(OH)_4] [H^+]^{-2}$ etc.

If the ionic product of water in 3 M Na(Cl) is K_w we get the relations, $*\beta_2 = \beta_2 K_w^2$ and $*K_2 = K_2 K_w$.

The formulas written for the germanate ions are based on the concept of four-coordination around germanium, but as usual the equilibrium data cannot distinguish between formulas with different content of solvent, such as GeO_3^{2-}, $GeO_2(OH)_2^{2-}$ and $Ge(OH)_6^{2-}$. Chemical symbols are in Roman, concentrations in italic type. Concentrations and equilibrium constants will be expressed in M (mole/l).

EXPERIMENTAL DETAILS

Reagents and analysis. Sodium chloride and sodium hydroxide were of p.a. quality and were standardized and purified by the usual methods of this laborarory [2,3].

The germanate solutions were prepared by dissolving weighed amounts of GeO_2 in sodium hydroxide as described in Ref. [1]. The germanium dioxide used was Johnson & Matthey specpure. We transformed it to the soluble form by heating it to 1130°C and then cooling it quickly.

Choice of experimental conditions. In order to reduce the liquid junction emf, E_j, we decided to use a medium of 3 M Na(Cl) instead of 0.5 m Na(Cl). For E_j in 3 M Na(Cl) we found the empirical relation, $E_j = 4.2 [OH^-]$ mV, where $[OH^-]$ is expressed in M. This relation may be compared with that for a 0.5 m Na(Cl)-medium [4], $E_j = 41 [OH^-]$ mV.

In order to find polynuclear complexes it is desirable to use as high germanium concentrations as possible. However, the low solubility of sodium germanate restricted the concentration range which could be investigated in the present work to $0.005 < B < 0.025$ M. Even with these low concentrations small amounts of the slightly soluble sodium germanate were precipitated from solutions which were left standing for a few days. The alkaline solutions used were apparently clear but showed a slight Tyndall effect. Like our earlier works [1,3,4] the present study was carried out as a number of potentiometric titrations. The measurements were carried out in an oil thermostat at 25°C. In each titration the hydroxide ion concentration $[OH^-]$ was varied, and the total germanium concentration, B, was kept constant. $[OH^-]$ was measured with a hydrogen electrode and since the analytical composition of the solution was known, the average number of OH^- bound per $Ge(OH)_4$ could be calculated from the relation,

$$Z = ([OH^-]_{tot} - [OH^-])/B$$

where $[OH^-]_{tot}$ is the analytical excess concentration of OH^- over $Ge(OH)_4$. With this definition Z is also equal to the average negative charge per germanium. The cell used in the emf measurements was,
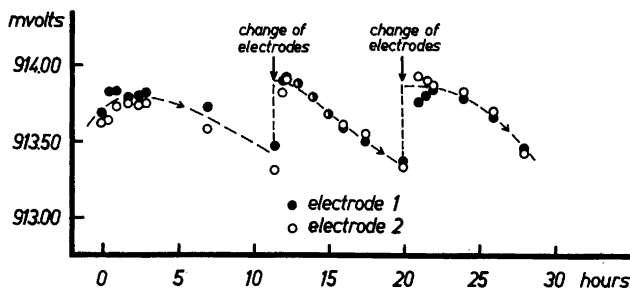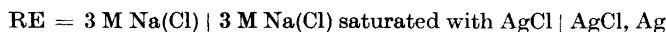
$$-Pt, \ H_2(1 \text{ atm}) \mid \text{germanate solution} \mid RE +$$
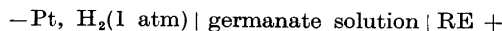
Fig. 1. The behavior of the hydrogen electrode in germanate solutions.

where

$$RE = 3 \text{ M Na(Cl)} \mid 3 \text{ M Na(Cl) saturated with AgCl} \mid AgCl, Ag$$

From the measured emf, E, we calculated [OH⁻] by using the relation,

$$E = E_o + 59.155 \log [OH^-] + E_j$$

where E_o is a constant and E_j the liquid junction emf. E_o and E_j have been determined in solutions without germanium and with known amounts of [OH⁻].

The behavior of the hydrogen electrode. In most of our titrations we started with a germanate solution with a composition very near to the precipitation range and added a more alkaline one. The measurements were carried out by using two hydrogen electrodes immersed in the germanate solution. The electrodes attained within 45 to 50 min, emfs which in general were the same within 0.1 to 0.2 mV. If not, they were immediately replaced with new ones. The emf. obtained in this way seemed to be constant during 15 − 20 min. However, by extending the measurements over longer periods we found that the emf decreased steadily by about 0.05 to 0.2 mV per hour. After say 5 h the emf had thus decreased by about 1 mV; if we then replaced both hydrogen electrodes with freshly prepared ones and measured once again, we obtained the initial value. This behavior of the hydrogen electrode is illustrated in Fig. 1, where the measured emf has been plotted against the time. The jumps in the curve show when old electrodes were replaced by new ones.

In some titrations we changed our electrodes after nearly every new addition of the alkaline solution of germanate. However, as we found that the decrease in emf per hour is nearly constant for a given electrode in a given experiment, we have in most of our titrations used a small time correction on the measured emf in order to get the initial emf. The magnitude of this correction was obtained by measuring the emf in the final solution both with the electrodes used during the titration and with freshly prepared electrodes. It is the "initial emf" which has been used for calculating [OH⁻].

One may think that the solutions contain small amounts of colloidal particles which slowly poison the hydrogen electrode. In order to prevent this the solutions were carefully filtered through a Jena Geräte G5-filter. However, this treatment did not affect the creeping of the electrode.

In attempts to check our emf values by back-titrations we found that the local excess of acid caused an initial precipitation of a germanate which redissolved very slowly.

RESULTS AND CONCLUSIONS

The experimental data from the present work are given as a set of values, $Z(\log [OH^-]_B$, in Table 1, and are plotted in Fig. 2. From Fig. 2 it is seen that Z is a function of [OH⁻] only, and that it is independent of the value of B.
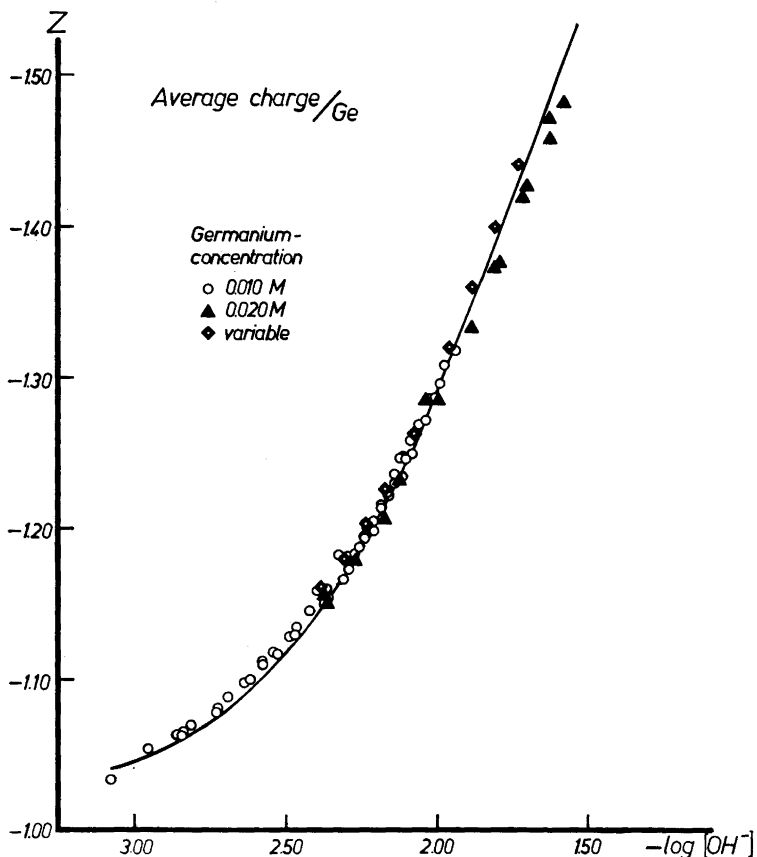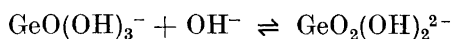
Fig. 2. Experimental data for germanates in 3.0 M Na(Cl).

This indicates formation of homonuclear complexes. Using graphical methods we found that data could be explained by the two mononuclear complexes, $GeO(OH)_3{}^-$ and $GeO_2(OH)_2{}^{2-}$ and for the reaction,

$$GeO(OH)_3{}^- + OH^- \rightleftharpoons GeO_2(OH)_2{}^{2-}$$

we found, log $K_2 = 1.64$. A refinement of the constants using the computer program, LETAGROP [15] gave the following "best" constants, log $K_2 = 1.64$.

In an attempt to see if our data contain any information of the constant K_1 (for the reaction, $Ge(OH)_4 + OH^- \rightleftharpoons GeO(OH)_3{}^-$) we used Letagrop and assumed the formation of $Ge(OH)_4$, $GeO(OH)_3{}^-$ and $GeO_2(OH)_2{}^{2-}$. This analysis showed that the error square sum was nearly independent of changes in the value of K_1 and we concluded that a determination of the constant K_1 is not possible from the present data. In order to get an accurate value of K_1 it

Table 1. Equilibrium data for germanates in 3.0 M Na(Cl).

$B = 0.010$ M; $-\log[OH^-], Z$; 2.8620, 1.063; 2.6957, 1.089; 2.5827, 1.112;
2.4012, 1.159; 2.3292, 1.182; 2.2783, 1.183; 2.2440, 1.195; 2.2135, 1.205;
2.1871, 1.215; 2.1432, 1.236; 2.1251, 1.247; 2.1251, 1.247; 2.0891, 1.259;
$B = 0.010$ M; $-\log[OH^-], Z$; 2.8637, 1.064; 2.6955, 1.089; 2.5789, 1.110;
2.4921, 1.128; 2.4245, 1.145; 2.3625, 1.155; 2.3141, 1.166; 2.2595, 1.188;
2.2088, 1.198; 2.1611, 1.221; 2.1180, 1.235; 2.0842, 1.249; 2.0226, 1.285;
$B = 0.010$ M; $-\log[OH^-], Z$; 3.0813, 1.034; 2.9574, 1.055; 2.8374, 1.065;
2.7283, 1.081; 2.6401, 1.098; 2.5466, 1.118; 2.4663, 1.135; 2.3731, 1.161;
2.2977, 1.182; 2.2360, 1.201; 2.1672, 1.224; 2.1139, 1.248; 2.0644, 1.269;
2.0279, 1.286; 1.9768, 1.308;
$B = 0.0097$ M; $-\log[OH^-], Z$; 2.8451, 1.063; 2.8145, 1.070; 2.7354, 1.079;
2.6235, 1.100; 2.5322, 1.117; 2.4730, 1.129; 2.3772, 1.151; 2.2960, 1.173;
2.2426, 1.193; 2.1871, 1.213; 2.1474, 1.231; 2.1052, 1.246; 2.0713, 1.263;
2.0402, 1.272; 2.0105, 1.286; 1.9907, 1.296; 1.9400, 1.318;
$B = 0.02005$ M; $-\log[OH^-], Z$; 2.3770, 1.155; 2.2730, 1.178; 2.1266, 1.232;
1.9958, 1.285; 1.8867, 1.332; 1.7948, 1.376; 1.7180, 1.419; 1.6289, 1.471;
$B = 0.02005$ M; $-\log[OH^-], Z$; 2.3677, 1.151; 2.1758, 1.206; 1.9604, 1.284;
1.8106, 1.372; 1.7050, 1.426; 1.6382, 1.458; 1.5773, 1.481;
B variable; B; $-\log[OH^-], Z$; 0.02005, 2.3878, 1.161;
0.02036, 2.3101, 1.180; 0.02068, 2.2397, 1.203; 0.02104, 2.1740, 1.226;
0.02166, 2.0798, 1.263; 0.02266, 1.9609, 1.320; 0.02345, 1.8844, 1.360;
0.02437, 1.8079, 1.400; 0.02542, 1.7336, 1.441;

would be necessary to go down to lower Z-values. However, using 3 M Na(Cl) as medium this is not possible due to the precipitation of a slightly soluble sodium germanate.

In Table 2 we have collected earlier obtained constants for mononuclear reactions of germanate ions. For all cases $*K_1$ and $*K_2$ are given and, if available, also the ionic product of water. Our constant K_2 has been recalculated to $*K_2$ using $pK_w = 14.07$ (determined in the present work). From this table we see that our $*K_2$-value (p$*K_2 = 12.43$) is higher than the $*K_2$-values (p$*K_2 = 12.72$ and 12.70) obtained by Pugh [6] (no salt medium) and Carpéni [7] (2 M KCl-medium) but lower than the values obtained in a medium of 0.5 m (molality) NaCl (Ingri [1]) and 0.5 M Na_2SO_4 (Thilo [8]) (these p$*K_2$-values are 12.24 and 12.31). As the $*K_2$-values given in Table 2 are obtained from measurements in different media no direct comparison of the values can be made. However, we may conclude that the $*K_2$-value of the present work is in satisfactory agreement with other emf investigations.

In the ranges studied, $-\log[H^+] > 11.5$ and $B < 0.020$ M, in the present work no indications of polyanion formation were found. In this respect germanium differs from its neighbor in the periodic system, silicon, which in the corresponding B- and pH-range clearly forms polysilicates [13].

The mononuclearity of germanate ions in strong alkaline solutions has also been reported in other investigations. Thus, Carpéni and Tchakirian [14] and Carpéni [7] concluded from emf work that the polyions formed at $-\log[H^+] = 8.8-9.2$ depolymerize at higher $-\log[H^+]$ to the monogermanate ions $GeO(OH)_3^-$ ($HGeO_3^-$) and $GeO_2(OH)_2^{2-}$ (GeO_3^{2-}).

Souchay [15], who used and extended the cryoscopic data of Roth and Schwartz [16] concluded from these measurements that germanate ions are

Table 2. Survey of earlier obtained equilibrium constants for mononuclear germanate species.

Author	Method	Medium	°C	$-\log {}^*K_1$	$-\log {}^*K_2$
Roth and Schwartz [16]	Conductance	dilute sol.	18	6.92	
Pugh [6]	emf, H_2-electrode	varied	20	8.59	12.72
Schwartz and Huf [9]	conductance	dilute sol.	20	7.30	—
Gulezian and Müller [10]	(conductance (colorimetry (pH-indicator)	(dilute sol. corrected to 0 corrected to 0	25 25 25	8.5 to 9.0 8.5 to 9.2 9.3 to 9.5 8.82 (average)	—
Carpéni [7]	emf, glass-electrode	2 M KCl	12	9.1	12.7
Lourijsen-Teyssèdre [11]	emf. glass-electrode	0.5 M Na_2SO_4	—	9.08	—
Antikainen [19]	emf. glass-electrode (the differential method)	extrapol	25	8.73	—
Krüger and Thilo [8]	H_2-electrode	Na_2SO_4, sat.	32	—	$12.31(pK_w = 13.66)$
Ingri [1]	emf, H_2- and glass-electrode	0.5 m Na(Cl)	25	$9.02(pK_w = 13.70)$	$12.24(pK_w = 13.70)$
The present work	emf, H_2-electrode	3.0 M Na(Cl)	25	—	$12.43(pK_w = 14.07)$

monomeric in alkaline solutions. Recent cryoscopic measurements by Thilo [8], using saturated sodium sulfate solutions also indicate mononuclear species in alkaline solutions where pH > 12.0.

Schwartz and Huf's dialysis experiments indicate monogermanate ions above pH $= 12.5$. Similar experiments by Brintzinger [17] also indicate the presence of monogermanate ions in strongly alkaline media (pH > 13). However, it has been found that dialysis experiments give questionable results in many cases and the method has in recent time been severely criticized.

Though the present work seems to be in good agreement with other investigations it is desirable that the measurements be extended to lower B-values and that both higher and lower Z-values be studied. A study of low B-values in the lower Z-range should be possible by means of the coulometer technique developed by Biedermann [18]. A study in the higher Z-range would be possible if one could find any electrode with a high accuracy at high $[OH^-]$. Studies in these directions are in progress.

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