Equilibrium Studies of Polyanions
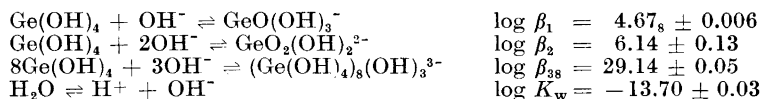
12. Polygermanates in Na(Cl) Medium

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The pH equilibria of germanic acid and germanate ion have been studied in 0.5 m (molality) Na(Cl) medium at 25°C by electrometric titration using a glass or a hydrogen electrode. The total germanium concentration, B, had values generally between 0.005 and 0.040 m. When the total germanium concentration B is $\leq$ 0.005 m, essentially only the mononuclear species germanic acid $Ge(OH)_4$ and the ions $GeO(OH)_3{}^-$ and $GeO_2(OH)_2{}^{2-}$ seem to be present; the data for $B > 0.005$ m give evidence also for a polynuclear species containing eight germanium atoms and with a charge minus three.
Reactions and constants:

$Ge(OH)_4 + OH^- \rightleftharpoons GeO(OH)_3{}^-$ $\log \beta_1 = 4.67_8 \pm 0.006$
$Ge(OH)_4 + 2OH^- \rightleftharpoons GeO_2(OH)_2{}^{2-}$ $\log \beta_2 = 6.14 \pm 0.13$
$8Ge(OH)_4 + 3OH^- \rightleftharpoons (Ge(OH)_4)_8(OH)_3{}^{3-}$ $\log \beta_{38} = 29.14 \pm 0.05$
$H_2O \rightleftharpoons H^+ + OH^-$ $\log K_w = -13.70 \pm 0.03$

The constants have been refined using the least squares program LETAGROP [1] and the error given is 3σ (σ is the standard deviation).

G ermanates has been studied far less extensively than silicates. However, what is known seems to indicate a close similarity between the chemistry of silicon and that of germanium which, we may remember, was the "ekasilicon" of Mendelejev.

In alkaline, aqueous solutions of silicates there are equilibria between silicic acid and various silicate ions. At high silicate concentrations polysilicates are also formed. In a recent study by Lagerström [2], of the silicate equilibria in 3.0 m (molality) and 0.5 m $Na(ClO_4)$, data were obtained which indicated that the main polynuclear complexes formed were tetra- and disilicate ions. In a subsequent work [3] it has been found that the same explanation may also be used for data obtained in 0.5 m Na(Cl). For a general mathematical analysis of silicate data (using the integration method [4]) it would be necessary to have more data, either in more acid solutions, from the wall corresponding to $Si(OH)_4$ upwards to more alkaline solutions; or, in more alkaline solutions, from the wall corresponding to, *e.g.*, $SiO_2(OH)_2{}^{2-}$ down-wards to more acid
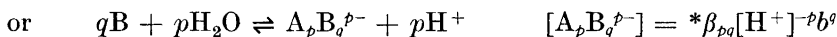
solutions. However, this is not possible. The ranges which up to now have been studied are limited, down-wards (more acid solutions) by the low solubility of $Si(OH)_4$, and up-wards by the accuracy of the emf measurement.

However, a study of the literature shows (see below) that germanic acid like silicic acid forms polyanions and is soluble over a wider concentration range than silicic acid. Thus in the case of the germanate equilibria it would be possible to use the general mathematical method [4] and so to find directly the composition of the polygermanate ions. We may hope that the similarity between the chemistry of germanium and silicon is so great, that the conclusions made for germanate might be valid for silicates too. In any event, it would also be of great value to know the differences.

<div align="center">SYMBOLS</div>

a $[OH^-]$; corresponds to reagent $A = OH^-$

b $[Ge(OH)_4]$; corresponds to reagent $B = Ge(OH)_4$

B total germanium concentration

$\mathcal{B}$ a normalized quantity corresponding to B

E the measured emf in mV

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

E_j $= \text{const} [H^+]$, liquid junction emf

H total analytical concentration of H^+ over $Ge(OH)_4$ and H_2O; H may be negative

P unique value for the number of A in A_PB_Q

p number of A in complex A_pB_q

$\bar{p}_{\text{poly}}$ average number of A per polynuclear complex

Q unique value for the number of B in A_PB_Q

q number of B in complex A_pB_q

$\bar{q}_{\text{poly}}$ average number of B per polynuclear complex

R^{-1} average degree of condensation of B

u a normalized quantity corresponding to a

v a normalized quantity corresponding to b

Z average number of A per B

Z' the intersection point

$\sigma(Z)$ standard deviation in Z as defined in Ref.[1]

$\sigma(\beta_{pq})$ standard deviation in β_{pq} as defined in Ref.[1]

The formation of a complex $A_pB_q{}^{p-}$ can be written

$$qB + pA^- \rightleftharpoons A_pB_q{}^{p-} \qquad\qquad [A_pB_q{}^{p-}] = \beta_{pq}a^p b^q$$

or $\quad qB + pH_2O \rightleftharpoons A_pB_q{}^{p-} + pH^+ \qquad [A_pB_q{}^{p-}] = {}^*\beta_{pq}[H^+]^{-p}b^q$

Between ${}^*\beta_{pq}$ and β_{pq} we have the following relation

$${}^*\beta_{pq}K_w{}^{-p} = \beta_{pq}$$

where K_w is the ionic product of water in 0.5 m Na(Cl).

Chemical symbols are in Roman, concentrations in italic type. Concentrations and equilibrium constants will be expressed in m or mm (moles or millimoles in 1000 g water).

A SHORT SURVEY OF THE CHEMISTRY OF GERMANATES

Structural and general chemistry. Like Si, Ge tends to surround itself with an oxygen tetrahedron. The GeO_4 tetrahedra may join to larger units through shared corners.

The similarity of Ge and Si is underlined by the fact that a large number of compounds of the two elements have proved to be isomorphous. A number of ortho-germanates, like Mg_2GeO_4 (high-temperature form) [5,6] and Zn_2GeO_4[6-8] are isomorphous with the corresponding silicates. Since the latter contains isolated SiO_4^{4-} groups, this proves the existence of isolated GeO_4^{4-} units in the solid phase. Chains of GeO_4 tetrahedra must exist in $CaMg(GeO_3)_2$[5] and Na_2GeO_3,[9] which are isomorphous with the corresponding Si compounds, and in $CuGeO_3$[10].

The three-dimensioned network of quartz is found in the water-soluble hexagonal form of GeO_2[11,12]. However, in contrast to SiO_2, there is a form of GeO_2 with six-coordination around germanium, namely the insoluble tetragonal form, which has the rutile structure [13].

Other known cases of six-coordination around Ge are analogous to Si: the hexafluorogermanate [14] ion GeF_6^{2-}, probably also the complex anions formed by Ge with certain ortho-diphenols [15] and the complex GeA_3^{+} with acetylacetone $(HA = CH_3COCH_2COCH_3)$ [16].

Since Ge is slightly larger than Si, one might imagine that the germanate ions in aqueous solutions might have an octahedral configuration, sometimes they are written $Ge(OH)_6^{2-}$. However, this formula seems to be unlikely since the salt SrH_2GeO_4 is isotypic with KH_2PO_4[17] and thus contains $H_2GeO_4^{2-}$ ions. One may note that recently isolated $Ge(OH)_6^{2-}$-groups have been found in the crystal structure of the mineral stoettite, $FeGe(OH)_6$. This mineral is isomorphous with $NaSb(OH)_6$ and $FeSn(OH)_6$[18].

According to Tchakirian and Carpéni [19] one can obtain from germanate solutions at pH $= 8 \rightarrow 10.2$, a crystalline precipitate, to which they give the formula $K_2Ge_5O_{11}$. This compound seems to have no silicate counterpart. The existence of the corresponding polyacid $H_2Ge_5O_{11}$ has been discussed [20,22] and in a recent work [21] also a compound has been prepared which is formulated $5GeO_2(H_2O)$.

Wittman and Nowotny [24] consider that the solids previously considered to be pentagermanates [19,23] are actually a heptagermanate "$Me_3HGe_7O_{16}$". These conclusions are based on X-ray (only powder photographs) data.

Shaw, Corwin and Edwards [25] found that by heating "$NaHGe_7O_{16}(H_2O)_4$" in a closed vessel at 200°C the compound $Na_4Ge_9O_{20}$[26] ($Na_2Ge_4O_9$) was formed. This work has later been confirmed [27] and a complete structure determination of this compound has been carried out [28]. In this enneagermanate, germanium is both six- and four-coordinated. The structures which are related to $Na_4Ge_9O_{20}$ are discussed in Refs.[27,28]

The compounds $Ge(SO_4)_2$[29], $Ge(ClO_4)_4$[30], $Ge_2(OH)_4Fe(CN)_6$[31] and $H_2Ge(C_2O_4)_3$[32] seem to have no known counterpart in silicon chemistry.

Two other differences from silicon chemistry are

1) Ge forms a rather stable bivalent ion, Ge^{2+}
2) $GeCl_4$ distils on heating a solution of GeO_2 in strong hydrochloric acid.

The organic compound of Ge have not been studied as extensivly as those of Si; the chemistry, however, seems to be analogous. For instance, rings of formula $(R_2GeO)_4$ have been found $(R = C_6H_5)$; $(R = C_2H_5)$ [33]. There are also high polymers of the formula $(R_2GeO)_\infty$; $(R = C_2H_5)$ [34].

Germanic acid forms anionic complexes with mannitol [35,36] and with carbohydrates [37] like boric acid. Perhaps silicic acid might also form such complexes if the proper conditions were chosen.

Mononuclear species in solution. The solubility of GeO_2 (hexagonal or melted) is more than 40 mM at 25° [38-40] as compared with about 2 mM for $Si(OH)_4$. The solution of GeO_2 in water has a normal freezing-point depression [41], indicating that the uncharged acid is present as a mononuclear species. From structural considerations [42,43] we may infer that it is $Ge(OH)_4$. Gulezian and Müller [44] found that the conductivity of $Ge(OH)_4$ solutions was independent of wether the solutions were prepared hot or cold, thus indicating that the equilibria should be rapid. However, Roth and Schwartz [41] observed that a solution that was prepared hot and then cooled, had a higher conductivity than one prepared cool. This is the only indication for slow equilibria. The explanation may be that there were some impurities in Roth and Schwartz solutions. By comparing the dissociation constants obtained by Roth and Schwartz with other values we find that their value is much higher (see below).

The dissociation constants for germanic acid, assumed to be mononuclear, have been estimated by several authors.

	pK_1		pK_2	
Roth and Schwartz (conductivity) [41]	6.92	(18°C)		
Pugh (H$_2$-electrode) [39]	8.59	(20°C)	12.72	(20°C)
Schwartz and Huf (conductivity) [40]	7.30	(20°C)		
Gulezian and Müller (conductivity, colorimetery) [44]	8.82	(average)		
		25°C		
Carpéni [20]	9.1	(12°C)	12.7	(12°C)
Lourijsen-Teyssèdre [45]	9.08			
Antikainen [46]	8.98	(15°C)		
	8.92	(20°C)		
	8.73	(25°C)		
	8.615	(30°C)		

However, for all concentrations, the shape of the pH titration curve for germanic acid is not exactly that expected for a simple dibasic acid. Moreover, if titration curves (or, Z *versus* pH curves) are plotted for different total concentrations of Ge, the curves are found to lie apart but to intersect at an average negative charge per Ge $Z \approx 0.36$ (0.40) (Z is also the average number of OH$^-$ bound to every Ge). This is a clear indication for formation of polynuclear complexes.

Polynuclear species in solution. The polynuclearity of species in alkaline germanate solution has been studied by Carpéni and coworkers [19-22]. They titrated germanate solutions using a glass electrode and kept the total germanium constant in every titration. The titration curves they obtained (the ordinate was "pH" and abscissa was the number OH$^-$ added per Ge, thus different from our Z) were interpreted by Carpéni [20] as evidence for the pre-

sence of the acid, $H_2Ge_5O_{11}$, with pK values of 6.2 and 7.8. Carpéni would thus assume the species H_2GeO_3, $HGeO_3^-$, GeO_3^{2-}, $H_2Ge_5O_{11}$, $HGe_5O_{11}^-$ and $Ge_5O_{11}^{2-}$.

Against this, Souchay [48] and Souchay and Teyssèdre [49,50] claim that the only polynuclear species one must assume is $Ge_5O_{11}^{2-}$.

Lourijsen-Teyssèdre[45] studied the germanate equilibria in 0.5 M Na_2SO_4 medium using a glass electrode. This work indicated mono and pentanuclear anions ($GeO(OH)_3^-$ and $Ge_5O_{11}^{2-}$) with pK values of 9.08 and -8.34.

Neither group seems to have made a complete comparison of calculated and observed pH values over the whole range and the conclusions are mainly based on the intersection point. If only $Ge_5O_{11}^{2-}$ is formed besides $Ge(OH)_4$, $GeO(OH)_3^-$ and $GeO_2(OH)_2^{2-}$, one should obtain a sharp intersection point at $Z = 0.40$ (see below). However, the data of the present work (see Fig. 1) and those of Carpéni and those of Lourijsen-Teyssèdre indicate an intersection point at $Z \approx 0.36$.

Wittman and Nowotny [24] proposed, mainly from the result of their X-ray investigations, that the polyanion in germanate solutions of pH $\approx$ 9 should be $HGe_7O_{16}^{3-}$ and not $Ge_5O_{11}^{2-}$. Similar views have been advanced by Shaw, Corwin and Edwards [25].

By ion exchange methods Everest and Salmon [51] found 1954 that concentrated germanate solutions contained the ion $Ge_5O_{11}^{2-}$. However, after the work of Wittman and Nowotny, Everest and Harrison reinvestigated the system and found that a heptagermanate ion must also be present and they proposed $H_2Ge_7O_{16}^{2-}$ mixed with $Ge_5O_{11}^{2-}$ and mononuclear ions.

From glass electrode measurements with concentrated $Ge(OH)_4$ solutions (prepared using ion exchanger) Antikainen [53] proposed the existence of a mixture of a dimer and a trimer both with the charge minus one. He gave the following constants: $\log*\beta_{12} = -4.3$ ($2B \rightleftharpoons H^+ + AB_2^-$) and $\log*\beta_{13} = -3.64$ ($3B \rightleftharpoons H^+ + AB_3^-$).

Conclusions from the literature. From the freezing point data of Roth and Schwartz [41] it seems likely that $Ge(OH)_4$ in acid solution is predominantly mononuclear. At low total germanium concentrations the germanate species in more alkaline solutions also seems to be mononuclear. We may write the mononuclear species, $Ge(OH)_4$, $GeO(OH)_3^-$ and $GeO_2(OH)_2^{2-}$. In strong alkaline solutions the germanate ions seem to be mononuclear at higher concentrations also [54]. In the intermediate range there must be polynuclear species, with a maximum around $Z = 0.36$.

However, the evidence for the formula $Ge_5O_{11}^{2-}$, like that of $HGe_7O_{16}^{3-}$, does not as yet seem convincing. In order to see wether these proposals are in agreement with the present data we will test them later in this publication.

It seems very desirable to obtain accurate data for germanic acid and to treat them in the way as we previously have used with boron [55,56]. With the germanium, it would be possible to obtain still more accurate results since the polynuclear species appear at much lower total concentrations than for borates.

EXPERIMENTAL

Reagents and analysis.
Sodium chloride, Merck p.a. was used. We found that this product was of high purity and could be used after drying at 350°C without further purification.
Hydrochloric acid. Kebo p.a., was standardized against KHCO₃ and standard NaOH. Gravimetrical determinations as AgCl always agreed within 0.2 %.
Sodium hydroxide was prepared and analysed as described in Part II [55]. In the hydrogen electrode measurements we used *commercial hydrogen*. Traces of oxygen in the hydrogen gas were removed using a column of activated Cu and the gas was washed as described in Part II [55].
Germanium(IV)oxide, Matthey & Johnson spec pure was used. This oxide was transformed to the soluble hexagonal form by igniting at 1130°C and then cooling quickly.

A p p a r a t u s

As in our earlier works [2,3,55] in alkaline solutions, Jena Geräte glass has been used for titration vessels and burets. The electrode vessel and the salt bridge were of the same type as described in Part II.[55] The glass electrode was of Beckman type and the emf values were read to ± 0.2 mV with a Radiometer pHM4 valve potentiometer. The hydrogen electrode and the silver reference electrode cell were prepared as described in Part II [55] and IV [3]. The cells including the titration vessel were kept in an oil thermostat at 25°C ± 0.1°C and the whole equipment kept in a thermostated room at 25°C. The solutions were introduced into the titration vessel either with a volume buret or a weight buret. The volume buret was calibrated by weighing water. The equilibrium solution was stirred by means of commercial nitrogen freed from O₂. The incoming gas passed through 10 % H₂SO₄, 10 % NaOH and 0.5 m NaCl.

P r e p a r a t i o n   o f   g e r m a n a t e   s o l u t i o n s

Acid Ge(OH)₄-solutions. Soluble GeO₂ was weighed out and dissolved in a weighed quantity of hydrochloric acid. Boiled distilled water was added in order to get the right germanium concentrations. After that, the amount of sodium chloride necessary to make [Na⁺] = 0.5 m (molality) was added.
Alkaline germanate solutions. In this case sodium hydroxide of known concentration was weighed out in a polythene vessel and a weighed quantity of GeO₂ was added. The desired amount of distilled boiled water was then added. After the GeO₂ had dissolved solid NaCl was added.
The germanium concentration in these solutions were checked in two cases by a gravimetric analysis. In this determination we carefully precipitated GeS₂ in strong sulfuric acid, filtered off the GeS₂ and transformed it to GeO₂ by oxidation using hydrogenperoxide in NH₃ solutions (See Ref.[57,58]). After igniting the hydrated GeO₂ at 900°C we weighed it out as GeO₂. The agreement with the calculated amount of GeO₂ and that one found in the analysis was always within 0.1 %.
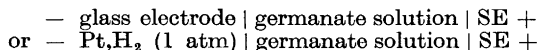
T h e   e m f   m e a s u r e m e n t s

In our measurements we have used a constant ionic medium in order to keep the activity factors as constant as possible so that concentrations might be used instead of activities in the law of mass action. As we shall study equilibria between negatively charged species we chose to keep [Na⁺] constant. We have used 0.5 m (molality) Na (Cl⁻, OH⁻) as medium and the concentration 0.5 m has been chosen because of the low solubility of germanate in more concentrated Na⁺-medium.
The determination of the equilibrium value for [H⁺] was made with a glass (mostly) or a hydrogen electrode in combination with the half-cell.

SE = 0.5 m NaCl | 0.5 m NaCl, saturated with AgCl | AgCl, Ag

The cell used was thus:

$$- \text{ glass electrode } | \text{ germanate solution } | \text{ SE } +$$
$$\text{or } - \text{ Pt,H}_2 \text{ (1 atm) } | \text{ germanate solution } | \text{ SE } +$$

Assuming the activity factors to be constant the emf of these cells may be written

$$E = E_{oh} - 59.155 \log[\text{H}^+] + E_j \tag{1}$$

where E_{oh} is a constant and E_j the liquid junction potential. The constant E_{oh} was determined before or after every titration in a solution containing Ge(OH)$_4$ and excess [H$^+$] (cf. Ref.[55]).

For the liquid junction potential we used $E_j \approx 83 \text{ [H}^+] \text{ mV}$ [3].

The experimental emf gave [H$^+$] (see eqn. 1), and the analytical composition of the solution gave B and H. H is the analytical excess concentration of hydrogen ions, H$^+$ assuming all germanium to be in the form Ge(OH)$_4$. From these quantities one could then calculate Z, the average number of OH$^-$ bound to Ge(OH)$_4$ from the relation.

$$BZ = [\text{H}^+] - H + K_w [\text{H}^+]^{-1} \tag{2}$$

where K_w is the ionic product of water in 0.5 m Na(Cl). We found $K_w = -13.70$.

The titration procedure and attainment of equilibria

In the present work the following titration procedures have been worked out and both have been used.

1) $Z(\log [OH^-])_B$-titrations. In these titrations the total concentration of germanium, B, has been kept constant and log [OH$^-$] and thus Z has been varied. The total hydroxide ion concentration was varied usually by increasing Z; then the solution in the titration vessel had $Z = 0$ and contained an excess H$^+$ over Ge(OH)$_4$; this solution was titrated with a more alkaline one with $Z \approx 1$. As Ge(OH)$_4$ is a rather weak acid the excess H$^+$, titrated in the first points of the titration can be used for checking the OH$^-$-concentration of the buret solution (using Gran's method [59]) and also for determination of E_{oh} and E_j.

In check titrations with decreasing Z the alkaline solution was in the titration vessel and the acid solution in the buret. The points so obtained were on the same titration curve as the others and and the equilibria were in both cases rapidly attained. In Table 1 these back-titrations are indicated.

2) $B(\log[OH^-])_Z$-titrations. In these titrations two ways for changing the total concentration of germanium have been used. In one of them the solution in the titration vessel was 0.5 m Na(Cl) and a solution with known Z and B was added; in the other way the solution contained the germanium (known Z and B) was kept in the titration vessel and 0.5 m NaCl was added by buret. From eqn. (1) and knowing that pH $\approx 5 \rightarrow 9$ it can be seen that during these titrations Z was nearly constant.

All these methods for getting experimental data have given consistent results and equilibrium was always rapidly obtained.

In most of our experiment we have used a glass electrode. In order to test this electrode also some measurements with the hydrogen electrode have been done. We found then that for "pH" < 9 the two electrodes always gave the same results. At higher "pH" the two electrodes deviated and in addition we found that the hydrogen electrode crept slowly (the solution seemed to become more acid). Compare this with the observation in Ref.[54] Points from the hydrogen electrode measurements in the stable range are collected in Table 1 and also plotted in Fig. 1.

In most of the titrations the glass electrode behaved normally. However, in some titrations, especially at low B values, the electrode seemed to jump in the unbuffered range around pH ≈ 5. The titration curve obtained after such a jump had the same shape as the other curves of the same concentration but was displaced on the log[H$^+$]-axis. These jumps were so frequent when we tried to titrate 0.0025 m that this concentration must be left out.
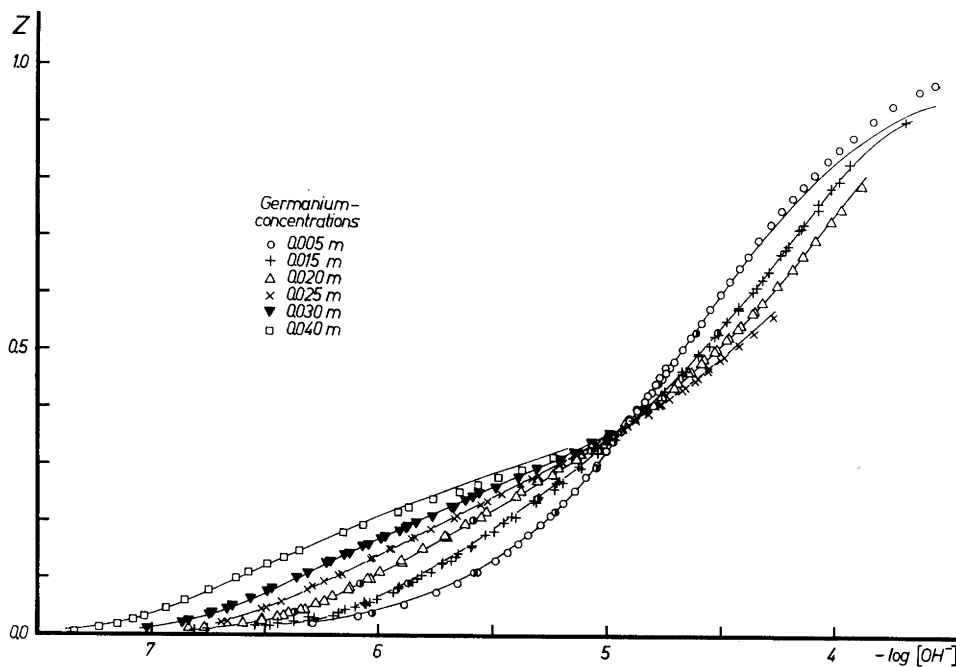
Fig. 1. Experimental data plotted as curves, $Z(\log[OH^-])_B$. The curves are calculated assuming formation of $GeO(OH)_3^-$ ($\log\beta_1 = 4.678$), $GeO_2(OH)_2^{2-}$ ($\log\beta_2 = 4.14$) and $(Ge(OH)_4)_8(OH)_3^{3-}$, $Ge_8O_{16}(H_2O)_5(OH)_3^{3-}$ ($\log \beta_{38} = 29.14$). The half-filled symbols represent titrations with hydrogen electrode.

SURVEY OF THE DATA

The primary experimental data, the emf values and the analytical composition of the solution, were recalculated using eqns. (1), (2) and K_w to give $Z(\log[OH^-])_B$. These data are given in Fig. 1 and Table 1.

The data, $\log B(\log[OH^-])_Z$, obtained by titrating at constant Z, are plotted in Fig. 2. The cuts, $\log B(\log[OH^-])_Z$, obtained from the set of curves, $Z(\log[OH^-])_B$, in Fig. 1 are also plotted in Fig. 2 for comparison.

From Fig. 1 we see that the curves, $Z(\log[OH^-])_B$, intersect, within a narrow range around $Z = 0.36 \pm 0.02$. Such an intersection was referred to as an isohydric point by Carpéni.

At $B = 0.040, 0.030, 0.025$, and 0.020 m, a sodium germanate is precipitated at some Z between 0.36 and 0.80, but dissolves again at higher Z-values. In the present work we have only investigated solutions with Z-values lower than corresponding to precipitation.

Due to the difference observed between the glass and the hydrogen electrode we will in our treatment of data mainly make use of data for $-\log[OH^-] > 4.3$. However, in our least squares treatment we will use also a few points for $-\log[OH^-] < 4.3$.

Table 1. Equilibrium data for germanates in 0.5 m Na(Cl). For the points used in LETAGROP $10^3(Z_{calc}-Z)$ is given. For calculating Z_{calc}, log $\beta_1 = 4.67_8$, log $\beta_2 = 6.14$, log $\beta_{38} = 29.14$ have been used.

$B = 0.040\ m$, Z, $10^3(Z_{calc}-Z)$: 7.3440, 0.0041, 3; 7.2358, 0.0106, 2; 7.1530, 0.0180, 1; 7.0888, 0.0255, 0; 7.0380, 0.0323, −1; 6.9434, 0.0461, −2; 6.8605, 0.0597, −3; 6.7557, 0.0775, −3; 6.6340, 0.0995, −2; 6.5799, 0.1091, −2; 6.4970, 0.1235, −1; 6.4227, 0.1361, 0; 6.3550, 0.1478, 1; 6.1606, 0.1803, 3; 6.0727, 0.1940, 4; 5.9205, 0.2173, 5; 5.8715, 0.2246, 5; 5.7684, 0.2400, 6; 5.6500, 0.2525, 11; 5.5706, 0.2640, 11; 5.4810, 0.2782, 10; 5.3745, 0.2934; 5.2409, 0.3145;

$B = 0.030\ m$, log [OH⁻], Z, $10^3(Z_{calc}-Z)$: 7.0262, 0.0105, 0; 6.8707, 0.0213; 6.7489, 0.0361, −2; 6.6762, 0.0459; 6.5697, 0.0641, −3; 6.4954, 0.0777; 6.3145, 0.1102, −2; 6.2164, 0.1287; 6.1302, 0.1445, 0; 6.0473, 0.1596; 5.9915, 0.1710, 0; 5.9104, 0.1847; 5.8377, 0.1986, 2; 5.7667, 0.2110; 5.6754, 0.2274, 3; 5.5892, 0.2446; 5.5411, 0.2615, 2; 5.3897, 0.2797; 5.3085, 0.2952, 1; 5.2240, 0.3110; 5.1462, 0.3241, 2; 5.0685, 0.3396; 4.9924, 0.3556, 0; 6.8419, 0.0241, 0; 6.7388, 0.0380; 6.6509, 0.0506, −3; 6.5714, 0.0638; 6.4734, 0.0820, −4; 6.3652, 0.1014; 6.2316, 0.1278, −3; 6.1538, 0.1420; 6.0727, 0.1570, −1; 5.9746, 0.1754; 5.8749, 0.1934, 0; 5.7802, 0.2104; 5.6839, 0.2277, 1; 5.6230, 0.2388; 5.5638, 0.2517;

$B = 0.025\ m$, log [OH⁻], Z, $10^3(Z_{calc}-Z)$: 6.6678, 0.0234, 2; 6.4970, 0.0472; 6.4311, 0.0565, 1; 6.2925, 0.0847; 6.1623, 0.1074, 1; 6.0372, 0.1330; 5.9476, 0.1511, 1; 5.8411, 0.1714; 5.6703, 0.2064, 3; 5.5232, 0.2349; 5.3271, 0.2765, 3; 5.1936, 0.3043; 5.0110, 0.3437, 5; 4.9298, 0.3634; 4.8757, 0.3778, 3; 4.7642, 0.4058; 4.6729, 0.4312, 4; 4.6137, 0.4474; 4.5579, 0.4656, 4; 4.4852, 0.4889; 4.4193, 0.5100, 5; 4.3533, 0.5308; 4.2705, 0.5607, −2; 6.6982, 0.0218; 6.5190, 0.0446, −1; 6.3145, 0.0788; 6.2434, 0.0926, 0; 6.1775, 0.1054; 6.0304, 0.1342; 5.9510, 0.1510; 5.8580, 0.1692, 2; 5.7718, 0.1860; 5.6568, 0.2095; 5.5537, 0.2303; 5.4624, 0.2488, 3; 5.3779, 0.2666; 5.3052, 0.2817; 5.2122, 0.3012, 3; 5.1141, 0.3218; 5.0465, 0.3378, 3; 4.9924, 0.3519; 4.9112, 0.3708; 4.8199, 0.3887; 4.7726, 0.4061, 1; 4.7270, 0.4157; 4.6577, 0.4355; 4.6019, 0.4517; 4.5562, 0.4696, 0; 4.5055, 0.4835;

$B = 0.020\ m$, log [OH⁻], Z, $10^3(Z_{calc}-Z)$: 6.7726, 0.0111, −1; 6.5207, 0.0228; 6.4227, 0.0327; 6.3314, 0.0443, 1; 6.2451, 0.0580; 6.1336, 0.0790; 6.0406, 0; 5.8986, 0.1261; 5.7075, 0.1724; 5.5554, 0.2069; 5.3998, 0.2437, 1; 5.2426, 0.2815; 5.1378, 0.3092; 4.9992, 0.3473; 4.8808, 0.3802, 0; 4.7980, 0.4042; 4.7084, 0.4343; 4.6323, 0.4605; 4.5883, 0.4776, −2; 4.5292, 0.4991; 4.4751, 0.5202; 4.4260, 0.5398; 4.3601, 0.5674, −2; 4.3195, 0.5851; 4.2519, 0.6152; 4.1860, 0.6442, 1; 4.1386, 0.6673; 4.0828, 0.6950; 4.0152, 0.7294, 3; 3.9696, 0.7498; 3.8800, 0.7921, 10;

$B = 0.020\ m$, −log [OH⁻], Z, $10^3(Z_{calc}-Z)$: 6.8419, 0.0100; 6.6036, 0.0188, −1; 6.5207, 0.0245; 6.4514, 0.0308; 6.4007, 0.0366, 0; 6.3483, 0.0434; 6.2806, 0.0541; 6.2079, 0.0671; 6.1319, 0.0811, −1; 6.0524, 0.0981; 5.9966, 0.1097; 5.9053, 0.1303, −3; 5.8090, 0.1521; 5.7109, 0.1742; 5.6247, 0.1940, −3; 5.5317, 0.2160; 5.3779, 0.2531; 5.3068, 0.2723, −5; 5.2156, 0.2941; 5.1395, 0.3133; 5.1158, 0.3198; 5.0719, 0.3317, −4; 5.0025, 0.3511; 4.9231, 0.3736; 4.8436, 0.3961, −4; 4.7625, 0.4196; 4.6915, 0.4435; 4.6441, 0.4606; 4.5765, 0.4847, −5; 4.5241, 0.5034; 4.4683, 0.5233; 4.4125, 0.5438; 4.3652, 0.5636, 0; (Back titration)

$B = 0.015\ m$, −log [OH⁻], Z, $10^3(Z_{calc}-Z)$: 6.0642, 0.0559, 2; 5.9087, 0.) 838; 5.8123, 0.1045; 5.7177, 0.1273; 5.5926, 0.1571, 5; 5.4522, 0.1983; 5.3204, 0.2367; 5.2189, 0.2675; 5.0008, 0.3377, 2; 4.8910, 0.3785; 4.7642, 0.4242; 4.6729, 0.4643; 4.5985, 0.4935, 1; 4.5275, 0.5262; 4.4734, 0.5526; 4.4227, 0.5763; 4.3584, 0.6053, 2; 4.2908, 0.6399; 4.2209, 0.6846; 4.1471, 0.7155; 4.0710, 0.7487, 9; 4.0152, 0.7874; 6.5461, 0.0156, −1; 6.3736, 0.0231; 6.3094, 0.0299; 6.1454, 0.0432, 3; 6.0609, 0.0544; 6.0068, 0.0633; 5.9138, 0.0808; 5.8292, 0.0991, 5; 5.7261, 0.1250; 5.6517, 0.1429; 5.5334, 0.1759, 3; 5.4184, 0.2091; 5.3001, 0.2431; 5.2105, 0.2719; 5.1260, 0.2983, 0; 5.0279, 0.3307; 4.9400, 0.3621; 4.8419, 0.3985, −2; 6.7557, 0.0100; 6.4463, 0.0190, 0; 6.2857, 0.0287; 6.1758, 0.0384; 6.1031, 0.0475, 6.0388, 0.0564; 5.9358, 0.0738, 7; 5.8495, 0.0927; 5.7701, 0.1099; 5.6602, 0.1370; 5.5959, 0.1545; 5.4945, 0.1817, 7; 5.3982, 0.2079; 5.3102, 0.2339; 5.1953, 0.2689; 5.1141, 0.2942; 5.0397, 0.3195; 4.9670, 0.3462, 5; 4.8977, 0.3703; 4.8318, 0.3948; 4.7506, 0.4289; 4.6695, 0.4589;

4.6002, 0.4915, 2; 4.5106, 0.5303; 4.4227, 0.5727; 4.3178, 0.6258; 4.2384, 0.6699; 4.1572, 0.7138; 4.0727, 0.7601, −3; 3.9299, 0.8295; 3.6872, 0.9062; 6.8166, 0.0073; 6.4801, 0.0158; 6.3111, 0.0240; 6.2012, 0.0329; 6.0558, 0.0524; 5.6822, 0.1298, 5.2308, 0.2569; 4.6543, 0.4652; 4.5528, 0.5091; 4.3449, 0.6121; 4.2147, 0.6789; 4.1352, 0.7226; 3.9780, 0.7998;

$B = 0.005\ m$, $-\log\,[OH^-]$, Z, $10^3(Z_{calc}-Z)$: 6.2925, 0.0189, 5; 6.0930, 0.0322; 5.8901, 0.0526, 5; 5.7498, 0.0737; 5.6568, 0.0903, 5; 5.5689, 0.1102; 5.4911, 0.1300; 5.4370, 0.1449, 4; 5.3897, 0.1598; 5.3474, 0.1756; 5.2933, 0.1938, 2; 5.2494, 0.2104; 5.1953, 0.2324; 5.1462, 0.2544, 0; 5.0955, 0.2777; 5.0482, 0.2989; 5.0059, 0.3240, −4; 4.9755, 0.3396; 4.9400, 0.3586, −5; 4.9062, 0.3810; 4.8707, 0.3978, −7; 4.8250, 0.4220; 4.7912, 0.4423; 4.7743, 0.4549, −10; 4.7456, 0.4710; 3.5571, 0.9727, −35; 3.6247, 0.9606; 3.7430, 0.9336; 3.8293, 0.9074, −27; 3.9172, 0.8781; 3.9797, 0.8564; 4.0304, 0.8358; 4.0913, 0.8111, −15; 4.1369, 0.7901; 4.1843, 0.7691; 4.2333, 0.7471, −10; 4.2806, 0.7227; 4.3347, 0.6953; 4.3804, 0.6674, −2; 4.4176, 0.6463; 4.4615, 0.6225; 4.5038, 0.5985, 1; 4.5511, 0.5742; 4.5883, 0.5492, 2; 4.6357, 0.5225; 4.6712, 0.5027, 1; 4.7083, 0.4819; 4.7253, 0.4720; 4.7439, 0.4623; 4.7608, 0.4522, 0; 4.7794, 0.4430; 4.8081, 0.4271; 4.8369, 0.4115; 4.8707, 0.3962, −5; 4.9028, 0.3791;

Hydrogen electrode titrations
$B = 0.005\ m$, $-\log\,[OH^-]$, Z: 4.612, 0.3348; 5.032, 0.2960; 5.232, 0.2179; 5.584, 0.1098; 6.028, 0.0382.
$B = 0.015\ m$, $-\log\,[OH^-]$, Z: 4.514, 0.5342; 5.312, 0.241; 5.874, 0.091;
$B = 0.020\ m$, $-\log\,[OH^-]$, Z: 6.375, 0.0391; 6.084, 0.0894; 5.590, 0.2014; 5.076, 0.3252;

TREATMENT OF EXPERIMENTAL DATA

From Fig. 1 we see that with decreasing B the curves, $Z(\log[OH^-]_B$, seem to approach a limiting curve. In order to see if this limiting curve is the same as that one for our lowest B (0.005 m) it would be desirable to have some curves, $Z(\log[OH^-])_B$ also for $B \leq 0.005$ m. As mentioned above we had difficulties with the glass electrode when we tried to get these curves.
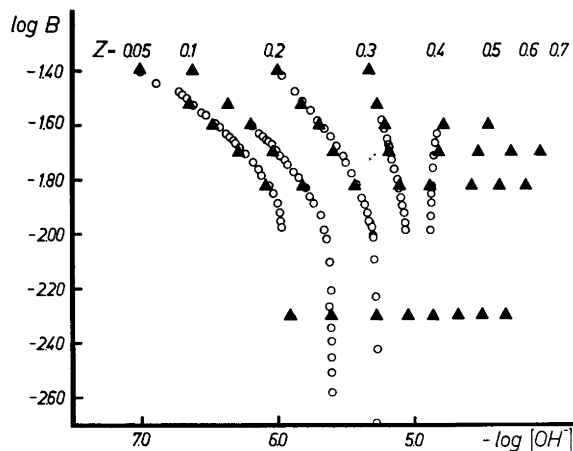

Fig. 2. Experimental data plotted as curves, log $B(\log[OH^-])_Z$. The filled triangles are points taken from cuts in Fig. 1; the other points have been obtained by titrations at constant Z (*cf.* text).

However, from titrations at "constant" Z considering only the range up to $Z \approx 0.7$ we concluded that the limiting curve was approximately the same curve, $Z(\log[OH^-])_B$, as that one for $B = 0.005$ m (See Fig. 2). We found that the shape of this curve was that one calculated for a normal diprotic weak acid. From the position on the $-\log[H^+]$ curve we found $\log K_1 = -9.03$ and $\log K_2 = -12.23$.

The fact that titrations for higher B give different curves, $Z(\log[OH^-])_B$, indicates for different B the formation of one or more polynuclear complexes.

In order to find the composition of these complexes we will start our analysis with the general integration method given by Sillén. In this method we get the mean composition of the polynuclear complexes, A_pB_q without any other assumption than that the law of mass action is valid and that the species where the integration starts is known.

On the basis of the results obtained by the integration method we will continue our analysis and test a number of probable complex combinations using graphical and least squares methods.

ELIMINATION OF THE MONONUCLEAR SPECIES, MEAN COMPOSITION OF THE POLYNUCLEAR COMPLEXES

From the experimental data, $Z(\log[OH^-])_B$, given in Table 1 and Fig. 1, we wish to calculate R^{-1}, the average degree of condensation of $Ge(OH)_4$, and b, the actual concentration of $Ge(OH)_4$. For this calculation we use the following two general equations given by Sillén [4].

$$R = R_o + \int_{Z_o}^{Z} \left(\frac{d \ln a}{d \ln B} \right)_Z dZ \qquad \text{at constant } B \qquad (3)$$

eqn. (19a) in Ref.[4]

$$\ln b = \ln b_o + (R - R_o) + \int_{a_o}^{a} Z \ d \ln a \qquad \text{at constant } B \qquad (4)$$

eqn. (21) in Ref.[4]

R_o is the R-value and b_o the concentration of $Ge(OH)_4$ where the integration starts. In the present system $R_o = 1$ and $b_o = B$.

Knowing the composition of the mononuclear curve, the contributions B_1 and B_1Z_1 of the mononuclear species in B and BZ may be calculated.

$$B_1 = b + \beta_1 ab + \beta_2 a^2 b; \quad (5a) \qquad\qquad B_1Z_1 = \beta_1 ab + 2\beta_2 a^2 b; \qquad (5b)$$

With these data the mean composition of the polynuclear complexes may be calculated from the relations.

$$\bar{q}_{poly} = \frac{B - B_1}{BR - B_1} \qquad (6a) \qquad\qquad\qquad \bar{p}_{poly} = \frac{BZ - B_1Z_1}{BR - B_1} \qquad (6b)$$

where $\bar{q}_{poly}$ is the average number of germanium atoms and $\bar{p}_{poly}$, the average charge of every polynuclear complex.

For the practical computation of $\bar{q}_{poly}$ and $\bar{p}_{poly}$ we have used the computer program MESAK (medelsammansättning av komplex) and the input

data in this case were Z, $\log[OH^-]$ and $(d \ln[OH^-]/d \ln B)_Z$. Z and $\log[OH^-]$ have been read off from the family of curves $Z(\log[OH])_B$ and the derivatives have been determined partly as described in Part 8 [60] and partly from the titrations at constant Z which give the derivative directly (cf. Fig. 2).

In MESAK instead of giving R_o and b_o we feed in the estimated values on $\bar{p}$ and $\bar{q}$ in the first point. If the guess was right the continuing curve $\bar{p}(\bar{q})_B$ was linear or slightly bend, others the curves had a sharp bend in the beginning.

The result of our integration is collected in Table 2. We found $\bar{p}_{poly} = 3 \pm 0.6$ and $\bar{q}_{poly} = 9 \pm 1.5$.

Table 2. Values for q_{poly} and p_{poly} obtained by the integration method [4].

$B = 0.040$ m

Z	p_{poly}	q_{poly}
0.05	3.2	7.1
0.10	3.2	8.5
0.15	3.2	8.9
0.20	3.1	8.6
0.25	2.8	7.8
0.30	2.7	7.5

$B = 0.030$ m

Z	p_{poly}	p_{poly}
0.05	3.6	9.5
0.10	3.7	9.2
0.15	3.8	9.2
0.20	3.5	9.5
0.25	3.3	9.0
0.30	3.2	8.6
0.35	3.2	8.6

$B = 0.025$ m

Z	p_{poly}	q_{poly}
0.05	2.2	5.9
0.10	2.7	7.5
0.15	2.9	8.1
0.20	2.9	8.0
0.25	2.9	7.9
0.30	2.9	7.8
0.35	2.9	7.8
0.40	2.9	7.9
0.45	2.9	8.0
0.50	2.8	7.7
0.55	2.5	7.3

$B = 0.030$ m

Z	p_{poly}	q_{poly}	Z	p_{poly}	q_{poly}
0.05	3.4	9.7	0.05	2.7	7.9
0.10	3.7	9.2	0.10	3.2	9.0
0.15	3.9	9.2	0.15	3.3	9.0
0.20	3.4	9.1	0.20	3.3	8.8
0.25	3.1	8.6	0.25	3.2	8.6
0.30	3.2	8.8	0.30	3.2	8.7
0.35	3.5	9.2	0.35	3.3	8.9
0.40	3.5	9.2	0.40	3.4	9.0
0.45	3.5	9.0	0.45	3.4	9.4
0.50	3.4	8.9	0.50	3.6	9.9
0.55	3.5	9.0			

THE INFORMATION FROM THE INTERSECTION POINT

From Fig. 2 we see that the curves, $Z(\log [OH^-])_B$ intersect around $Z = 0.36 \pm 0.02$. It is impossible to say if the curves intersect in a single point or within a range.

However, one may ask what it would imply if the curves intersect exactly in a single point. The condition for this is that for some value of a, Z is independent of b.

Using the law of mass action and the conditions for the concentrations we may write for a case where mononuclear species, A, AB and A_2B are present besides one or more polynuclear complexes A_pB_q,

$$Z = \frac{\beta_1 ab + 2\beta_2 a^2 b + \sum_p \sum_q p\beta_{pq} a^p b^q}{b + \beta_1 ab + \beta_2 a^2 b + \sum_p \sum_q q\beta_{pq} a^p b^q} \tag{7}$$

This expression for Z is valid for all B-values. For low concentrations when mainly B, AB and A_2B are present we may write (7)

$$Z = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} \tag{8}$$

If the curves intersect in a single point, Z', we may write

$$Z' = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} = \frac{\beta_1 ab + 2\beta_2 a^2 b + \sum_p \sum_q p\beta_{pq} a^p b^q}{b + \beta_1 ab + \beta_2 a^2 b + \sum_p \sum_q q\beta_{pq} a^p b^q} \tag{9}$$

Rearranging this expression we get

$$(\beta_1 a + 2\beta_2 a^2) \sum_p \sum_q q\beta_{pq} a^p b^q = (1 + \beta_1 a + \beta_2 a^2) \sum_p \sum_q p\beta_{pq} a^p b^q \tag{10}$$

or

$$Z' = \frac{\sum_p \sum_q p\beta_{pq} a^p b^q}{\sum_p \sum_q q\beta_{pq} a^q b^q} \tag{11}$$

From eqn. (11) we see that the condition for all the Z curves to intersect in a single point is that for some value of a, Z is independent of b. This could be exactly fulfilled if there were only one value for q represented; if there were one polynuclear complex $A_P B_Q$ besides the mononuclear ones $A_p B$ thus eqn. (11) is reduced to

$$Z' = P/Q$$

We have experimentally found $Z' = 0.36 \pm 0.01$ and if only one polynuclear complex $A_P B_Q$ is present the following $A_P B_Q$-complexes are possible, A_3B_8, A_4B_{11}, A_5B_{14} and so on.

If two polynuclear complexes were present e.g. AB_5^- and $A_2B_5^-$ one would expect an intersection point between the two extreme values, $1/5$ and $2/5$ and from eqn. (11) and Z' we may get the ratio between the constants. $\beta_{15}/\beta_{25} = a(5Z'-2)(1-5Z')^{-1}$.

SOME PROJECTION MAPS FOR TESTING FORMATION OF A SINGLE POLY-NUCLEAR COMPLEX, $A_P B_Q$

Assuming formation of only one polynuclear complex $A_P B_Q ((OH)_P (Ge(OH)_4)_Q)$ besides B $(Ge(OH)_4)$, AB $(GeO(OH)_3^-)$ and A_2B $(GeO_2(OH)_2^{2-})$ the law of mass action and the conditions for the concentrations give

$$B = b + \beta_1 ab + \beta_2 a^2 b + Q\beta_{PQ} a^P b^Q \tag{12}$$
$$BZ = \beta_1 ab + 2\beta_2 a^2 b + P\beta_{PQ} a^P b^Q \tag{13}$$

where $a = [OH^-]$ and $b = [Ge(OH)_4]$.

We wish to normalize these expressions to

$$B = v + uv + lu^2 v + Qu^P v^Q \tag{14}$$
$$BZ = uv + 2 lu^2 v + Pu^P v^Q \tag{15}$$

This is achieved by the substitutions

$$u = \beta_1 a \quad (16a); \qquad v = b(\beta_{PQ}\beta_1^{-P})^{1/(Q-1)} \quad (16b); \qquad B = B(\beta_{FQ}\beta_1^{-P})^{1/(Q-1)} \quad (16c)$$

The constant $l = \beta_2\beta_1^{-2}$.

With (14) and (15) it is possible to calculate $\log B$ as a function of Z and $\log u$ for different PQ-combinations. For the practical computation of these maps we have used the computer program HALTABI. We started the calculation with the following PQ-values: 2.5; 3.7; 3.8 and 4.11. The combination with 2.5 has been proposed among others by Carpéni[20] and Souchay[48] and 3.7 by Wittman and Nowotny[24]. The combinations 3.8 and 4.11 give an intersection point around the experimentally found value $Z = 0.36 \pm 0.02$. These calculated maps, $\log B(\log[OH^-])_Z$, are in Fig. 3 compared with the experimental $\log B$ (log $[OH^-])_Z$ data. They are given in the position of best fit and the difference in reading along the coordinate axes on the experimental and calculated graphs gives the constants β_1 and β_{PQ}

$$\log B - \log B = (Q-1)^{-1} (\log \beta_{PQ} - P \log \beta_1) \tag{16}$$

$$\log u - \log a = \log \beta_1 \tag{17}$$

The value of l used in the calculation was $6.03 \cdot 10^{-4}$.

From Fig. 3 we see that the PQ-pairs which fit best with data are 3.8 and 4.11. The combinations with 2.5 and 3.7 give a poor fit and we consider that no one of them can explain the present data.

Using (16) and (17) and $l = 6.03 \cdot 10^{-4}$, we found for the two combinations A_3B_8 and A_4B_{11} the following equilibrium constants:

$$\log \beta_1 = 4.68 \pm 0.05 \quad \log \beta_2 = 6.14 \pm 0.20 \quad \log \beta_{38} = 29.18 \pm 0.05$$
$$\log \beta_1 = 4.68 \pm 0.05 \quad \log \beta_2 = 6.14 \pm 0.20 \quad \log \beta_{4.11} = 40.36 \pm 0.05$$

The agreement between calculated and experimental $\log B(\log a)_Z$ data is very good for both A_3B_8 and A_4B_{11} and we think that with projection maps it is not possible to make a choice between them and select the "best" one. For this purpose we must use some other method, e.g. the least squares method using LETAGROP[1].

PQ ANALYSIS USING THE LEAST SQUARES PROGRAM, LETAGROP.

From the computation using MESAK we found that the mean composition of the polynuclear complexes is around $A_{3.5}B_9$. In the present section we will use the computer program LETAGROP and test some of those combinations with polynuclear complexes A_PB_Q, that "best" explain our experimental data. For every combination tested LETAGROP adjust the equilibrium constants so that the error square sum, $\Sigma(Z_{calc} - Z_{exp})^2$ is as low as possible. We consider that the "best" combination is that one which, with the same points, gives the lowest error square sum, $\Sigma(Z_{calc} - Z_{exp})^2$. For the calculation we have picked out from the data given in Table 1, at random 120 points (20 points from every B).

1) At *first* we assumed that only *one polynuclear complex* A_PB_Q exists besides the mononuclear ones, AB $(GeO(OH)_3^-)$ and A_2B $(GeO_2(OH)_2^{2-})$. The different PQ-pairs tested and the error square sums are collected in the *pq-*
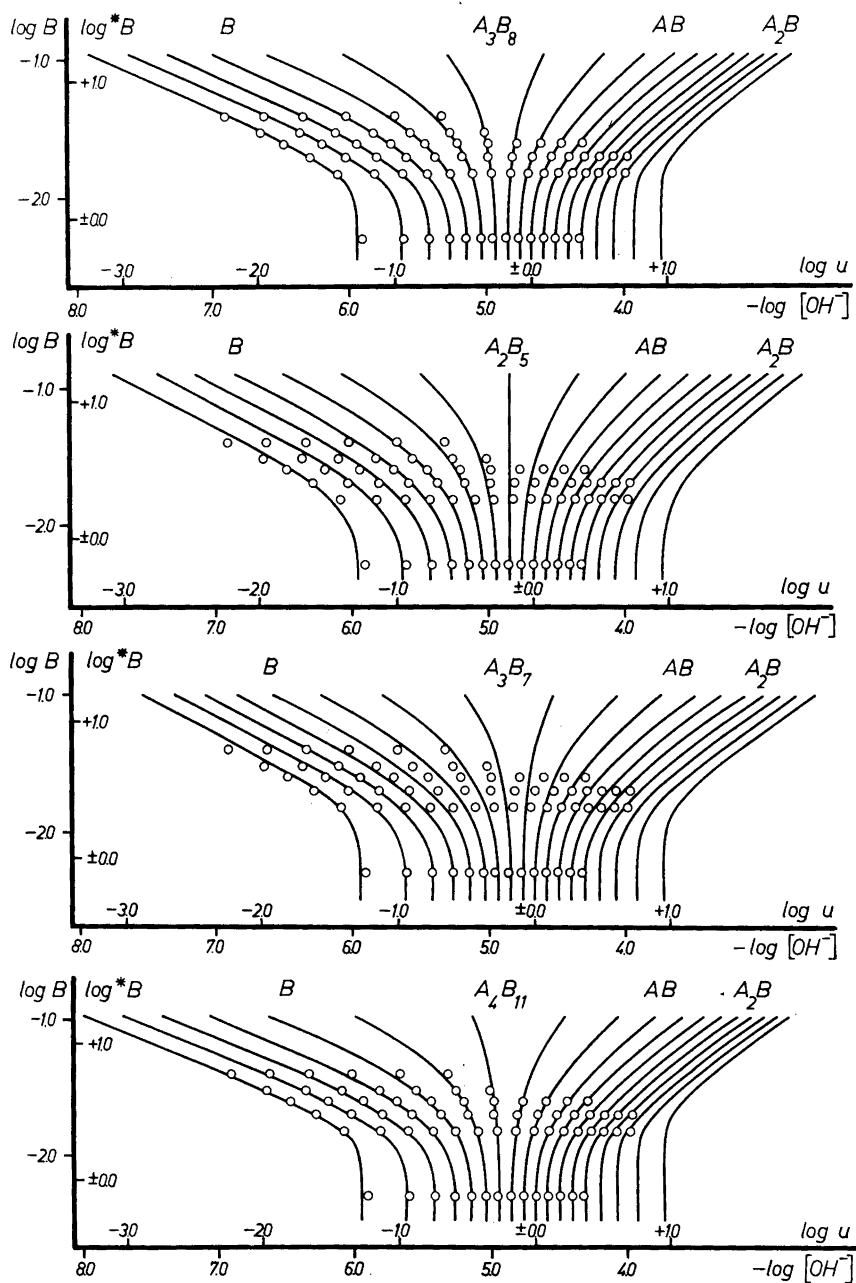
Fig. 3. Projection maps in position of best fit, calculated for the following species:
1) B, AB, A$_2$B and A$_3$B$_8$ (main conclusion of the present work)
2) B, AB, A$_2$B and A$_2$B$_5$ (the hypothesis of Carpéni [20] and Souchay [48])
3) B, AB, A$_2$B and A$_3$B$_7$ (the hypothesis of Wittman and Nowotny [24])
4) B, AB, A$_2$B and A$_4$B$_{11}$ (give a good fit)
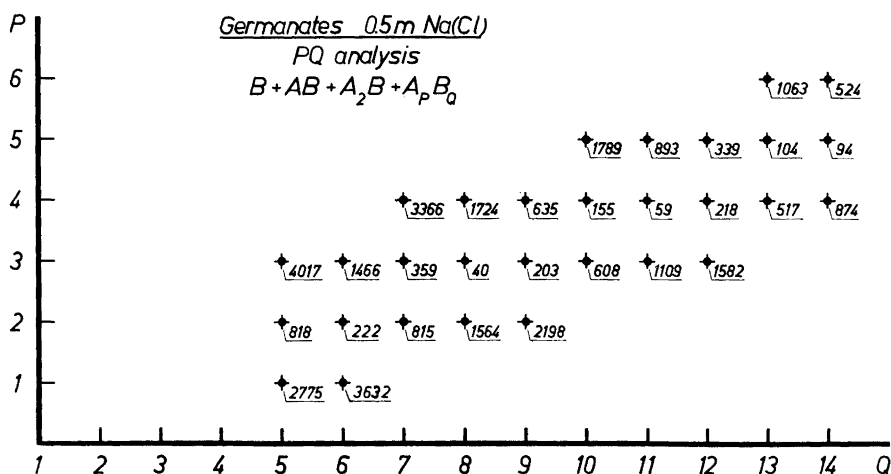
Fig. 4. Error square sums for some PQ pairs assuming formation of AB, A_2B and A_PB_Q.

diagram in Fig. 4. In Table 3 the equilibrium constants and the standard deviations, $\sigma(Z)$ are collected for the combinations which gave low error square sums. From this analysis we found that the combination containing the polynuclear complex $\overset{\cdot}{A}_3B_8$ $((OH)_3(Ge(OH)_4)_8)$ gave the lowest square sum. We found the following equilibrium constants and errors (given as 3 σ), $\log \beta_1 = 4.67_8 \pm 0.006$, $\log \beta_2 = 6.14 \pm 0.13$ and $\log \beta_{38} = 29.14 + 0.05$.

Other PQ-pairs which also give low error squares sums are 4.11, 5.14 and 6.17. Of these combinations 4.11 has the lowest error square sum. The standard deviations in $Z, \sigma(Z)$ are in these two cases 0.0059 and 0.0071, respectively. By comparison of calculated and experimental data we found systematical deviations for 4.11 compared with 3.8. $\varDelta Z = 10^3(Z_{calc} - Z_{exp})$ for the combination with 3.8 are given in Fig. 5.

Thus the PQ-analysis with the simple assumption that only the polynuclear complex A_3B_8 is formed seems to be a satisfactory explanation of the present data. This is also in agreement with the result obtained using the integration method.

Table 3. Letagrop analysis of germanate data. Constants obtained for the "best" PQ pairs assuming formation of AB, A_2B, and A_PB_Q. $\sigma(Z)$ is the standard deviation in Z.

PQ in A_PB_Q	$\log\beta_1$	$\log\beta_2$	$\log\beta_{PQ}$	$\sigma(Z)$
3.8	4.678	6.141	29.135	0.0059
4.11	4.677	6.123	40.440	0.0071
5.14	4.677	6.109	51.776	0.0090
5.13	4.674	6.138	49.752	0.0095
3.7	4.667	6.169	27.088	0.0177
2.5	4.674	6.170	17.879	0.0266

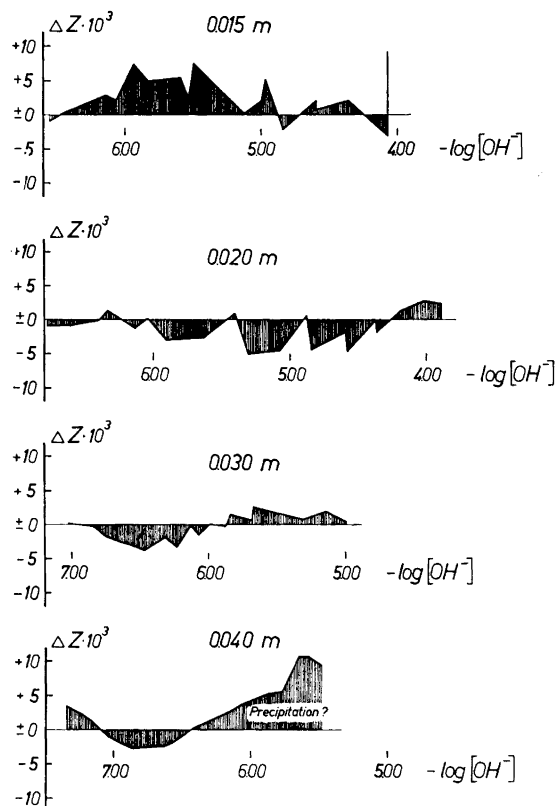*Fig. 5.* $\Delta Z = 10^3(Z_{calc} - Z_{exp})$ *versus* log[OH]. Z_{calc} has been calculated using $\log\beta_1 = 4.67_8$, $\log\beta_2 = 6.14$ and $\log\beta_{38} = 29.14$ (our main conclusion).

2) *Next,* one would like to assume that *two polynuclear complexes* are formed besides AB and A_2B. However, this assumption gives such a great number of possibilities that all of them cannot be tested. One should like to start this calculation by testing two "adjacent" (in the *PQ* diagram) poly-nuclear complexes which give an intersection point at $Z \approx 0.36$, *e.g.* $B_2 + AB_2$, $AB_3 + A_2B_3$, $AB_4 + A_2B_4$, $AB_4 + A_2B_5$ and so on; and $AB + AB_3$, $A_2B_5 + A_2B_6$ and so on. The combinations may be reduced further if we consider that the mean composition of complexes must be around $A_{3.5}B_9$. However, these calcula-tions have not been carried out.

In the future when more computing time and computers with higher cal-culating speed are available we hope that it will be possible to test these com-binations also. It is very probable that by such a calculation we might find combinations with square sums lower than that found for A_3B_8. Such a result need not necessary mean that the complexes in the "better" combination should be preferred to A_3B_8. We think that by assuming more and more com-plexes and give them suitable formation constants the square sum must neces-sarily go down and a better and better fit be obtained.
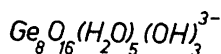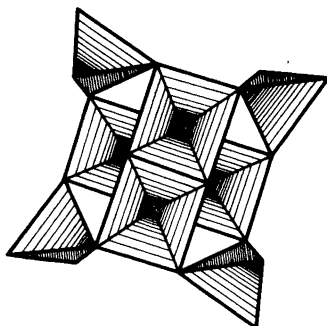
$$Ge_8O_{16}(H_2O)_5(OH)_3^{3-}$$

Fig. 6. Possible structure for the ion $A_3B_8{}^{3-}$. The ion has been cut out from the structure of $Na_4Ge_9O_{20}$ (*cf.* Ref.[28]) and should then have the formula $A_3B_8{}^{3-} = Ge_8O_{16}H_{13}{}^{3-}$, perhaps arranged as $Ge_8O_{16}(H_2O)_5(OH)_3{}^{3-}$.

CONCLUSIONS

The present data indicated that by adding OH^- to $Ge(OH)_4$ solutions the anions $GeO(OH)_3{}^-$, $GeO_2(OH)_2{}^{2-}$ and $(OH)_3(Ge(OH)_4)_8{}^{3-}$ are formed. Their formation constants are collected in Table 3. The assumptions that $Ge_5O_{11}{}^{2-}$ or $HGe_7O_{16}{}^{3-}$ (previous proposals) should be formed instead of $(OH)_3(Ge(OH)_4)_8{}^{3-}$ have been tested with the least square program LETAGROP. We find that neither of them can explain our data.

One may ask if it is possible to give the polyanion $(OH)_3(Ge(OH)_4)_8{}^{3-}$ a reasonable structural interpretation. However, data which give information about structures in solution are lacking. In such a case one may guess from what is known of the solid state and assume that $Ge(IV)$ forms the same type of units or at least has the same coordination number in solutions as in the solid. One may note that an equilibrium study like the present one can give no information on the structure but only on the number of Ge and the charge of the polynuclear complexes.

From the structural work of Wittman and Nowotny [24] ($Na_3HGe_7O_{16}(H_2O)_4$) and from our own X-ray work [28] on $Na_4Ge_9O_{20}$ we propose that the eight germanium atoms in the polyanion, $A_3B_8{}^{3-}$ may be arranged and connected as shown in Fig. 6.

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The Crystal Structure of $Na_4Ge_9O_{20}$

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Crystals of $Na_4Ge_9O_{20}$ are tetragonal, space group $I4_1/a$, with the dimensions $a = 14.98 \pm 0.01$ Å, $c = 7.384 \pm 0.005$ Å. The unit cell contains four formula units. Using three-dimensional Patterson and Fourier methods the germanium, oxygen and sodium positions have been determined. These positions have been refined using the method of least squares. The refined atomic coordinates are collected in Table 2. $Na_4Ge_9O_{20}$ is built up of GeO_4 tetrahedra and GeO_6 octahedra coupled together forming a three-dimensional network. (*cf.* Figs 2 a, b, and c). The Ge—O distances have been determined with a standard deviation of ± 0.015 Å. Table 3 gives the most important distances and angles in the structure. The mean Ge—O distance for octahedral coordination is 1.90_7 Å (in the structure varying from 1.82_2 Å to 1.99_8 Å) and for tetrahedral coordination 1.74_3 Å (in the structure varying from 1.71_5 to 1.76_4 Å).

I n a previous paper [1] we described the preparation of crystalline $Na_4Ge_9O_{20}$, gave its crystallographic data and its germanium parameters. The aim of the present work is to determine the positions of the oxygen and sodium atoms and to refine the structure.

$Na_4Ge_9O_{20}$ was made by heating precipitated sodium germanate with its mother liquid (pH $\approx$ 9) in a closed vessel at 300°C. Using single crystals prepared in this way, Weissenberg photographs ($hk0—hk3$, $0kl—6kl$, $hhl—h$, $h + 7, l$) were taken, using CuK radiation. The cell dimensions of the tetragonal unit cell were found to be: $a = 14.98$ Å $c = 7.384$ Å. The characteristic space group is $I4_1/a$, No. 88 in the International Tables [2]. The unit cell contains four formula units ($Na_4Ge_9O_{20}$) giving a calculated density of 4.268 g.cm^{-3} as compared with our observed value of 4.19 g.cm^{-3}.

The intensities of the reflexions were estimated visually using the multiple films technique and a calibrated scale. Lorentz and polarization corrections were made according to Lu [3]. No correction was made for the absorption. In this way the $|F_o|$ values of 693 independent, observed reflexions were obtained (*cf.* Table 1).

From a series of Patterson calculations we could determine the positions of the 36 germanium atoms in the unit cell.[1] We found: