

## Multicomponent Polyanions

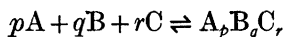
### III. A Potentiometric Study of Germanate—Mannitol Equilibria in 0.5 M Na(Cl) Medium

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Equilibria between  $\text{H}^+$ ,  $\text{Ge}(\text{OH})_4$ , and D-mannitol ( $\text{C}_6\text{H}_{14}\text{O}_6$ ) have been studied in 0.5 M Na(Cl) medium at 25°C by means of potentiometric (glass electrode) measurements. The pH-range 2–9 has been covered. All data could be explained with the ternary complexes  $(\text{H})_{-1}(\text{Ge}(\text{OH})_4)(\text{C}_6\text{H}_{14}\text{O}_6)^-$  and  $(\text{H})_{-1}(\text{Ge}(\text{OH})_4)(\text{C}_6\text{H}_{14}\text{O}_6)_2^-$  together with a small amount of an additional complex  $(\text{H})_{-2}(\text{Ge}(\text{OH})_4)_2(\text{C}_6\text{H}_{14}\text{O}_6)_2^{2-}$ . The existence of the first two species seems to be well established whereas the existence of the third is questionable. Data have been treated using the least squares computer program LETAGROPVRID. "Best" equilibrium constants and standard deviations are collected in Table 2.

In a series of investigations in progress in this department we are studying three component polyanion equilibria:



In the present report we will present an investigation of the system  $\text{H}^+$ - $\text{Ge}(\text{OH})_4$ -mannitol; thus A, B, and C stands for  $\text{H}^+$ ,  $\text{Ge}(\text{OH})_4$ , and mannitol, respectively. The aim is to obtain a quantitative description of the equilibria in the system. It is an experimentally rather easy system. The study may provide an evaluation of the method, and would give a basis for further studies in other similar systems, *e.g.* in systems with borate and silicate ions.

#### PREVIOUS WORK

Complex formation between germanic acid and mannitol was first reported by Tchakirian<sup>1</sup> in 1928. He observed that the solubility of  $\text{GeO}_2$  in water was increased by the addition of mannitol and that the pH of the solution decreased by formation of acids which are much stronger than germanic acid itself. He found that the acids formed consumed one  $\text{OH}^-$  per germanium

and proposed the formula  $H_2[Ge_2O_5(Ma)_n]$  with  $n \geq 2$ . Mannitol will in the following often be denoted Ma. The Ge-Ma acids soon found use in the analytical determination of germanium.<sup>2-6</sup>

Only a few investigators have studied the germanium-mannitol system thoroughly. Antikainen<sup>7</sup> found (from potentiometric investigations, 25°C, 0.1 M KCl), that only one singly charged complex is formed with a Ge-Ma ratio of 1:2 and with a formation constant of  $10^{-4.050}$ . Nazarenko and Flyantikova<sup>8</sup> came to the same result by means of pH measurements (a molar ratio method). Like Antikainen they used an excess of mannitol. They determined the thermodynamic ionization constant (25°C) by means of an indicator method (using a spectrophotometer) and obtained the value  $(1.21 \pm 0.01) \times 10^{-5}$ . Everest and Harrison<sup>9</sup> studied the Ge-Ma system in the pH-range 3-12 by using ion-exchange resins. They proposed complexes with Ge-Ma ratios of 1:1, 1:2, and 1:3 with charges -1, -2, and -2, respectively. They also found indications for an uncharged 1:1, a singly charged 1:2, and a singly or doubly charged polynuclear complex. The authors also make suggestions for the structures of the various species.

The existence of a complex with a Ge-Ma ratio of 1:2 seems to be well established when excess of mannitol is used. However, at low Ma-Ge ratios other complexes appear probable, the compositions of which are rather uncertain. It thus seems worthwhile making a more general investigation by taking all three components into consideration.

## EXPERIMENTAL

*Chemicals and analyses.* Sodium chloride, sodium hydroxide, and germanium dioxide were prepared and analysed as described by Ingri<sup>10</sup> and D-mannitol as described by Pettersson.<sup>11</sup> Hydrochloric acid, Merck *p.a.*, was standardized against  $KHCO_3$  or tris-hydroxymethylaminomethane (TRISMA-base).

*Apparatus.* The emf equipment and arrangement used were the same as described by Sjöberg.<sup>12</sup>

*Coulometric (OH<sup>-</sup>)-addition.* In titrations with low B concentrations (2.5 and 5.0 mM), OH<sup>-</sup> was added by using a coulometer with the following cell-arrangement:



cathode reaction:  $H^+ + e^- \rightleftharpoons 1/2 H_2(g)$

anode reaction:  $Ag(s) + Cl^- \rightleftharpoons AgCl(s) + e^-$

The coulometer used was a Metrohm type E 211.

## Method

The present study has been carried out as a series of emf titrations at 25°C and in 0.5 M Na(Cl) medium. In each titration the total concentrations of germanium, *B*, and mannitol, *C*, have been kept constant and  $[H^+] = h$  has been varied by the addition of OH<sup>-</sup> or H<sup>+</sup>. *B* and *C* have been varied within the limits  $2.5 \text{ mM} \leq B \leq 30 \text{ mM}$  and  $5 \leq C \leq 320 \text{ mM}$ . The free hydrogen ion concentration, *h*, has been measured with a glass electrode with an accuracy of  $\pm 0.2 \text{ mV}$ . The range of pH ( $= -\log h$ ) has been kept within the limits  $2 < \text{pH} < 9$ .

The free H<sup>+</sup>-concentration was determined by measuring the emf of the cell



Assuming the activity coefficients to be constant the following expression is valid for the measured emf:

$$E = E_0 + 59.157 \log h + E_j \quad (1)$$

$E_0$  is a constant that could be determined in every titration in the acid range where the binary and ternary reactions can be neglected. For the liquid junction potential,  $E_j$ , we have used  $E_j = -83 h + 41 K_w h^{-1}$  (mV), where  $K_w = 2.0 \times 10^{-14} \text{ m}^2$  (the ionic product of water in 0.5 m NaCl),<sup>13,14</sup>

From  $h$ , calculated by using eqn. (1), and from  $H$ , the excess concentration of hydrogen ions over the zero level  $\text{Ge}(\text{OH})_4$ , mannitol, and  $\text{H}_2\text{O}$ , one can calculate  $Z$ , the average number of  $\text{H}^+$  bound per  $B$ , using the relation:

$$Z = (H - h)/B \quad (2)$$

*Equilibria, the law of mass action and the conditions for the concentrations.* In the present study in addition to the three component equilibria:



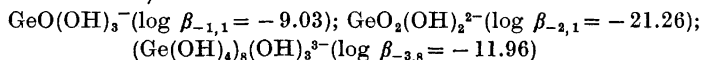
we need to consider the binary equilibria:



In eqns. (3) and (4)  $A = \text{H}^+$ ,  $B = \text{Ge}(\text{OH})_4$ , and  $C = \text{mannitol} (\text{C}_6\text{H}_{14}\text{O}_6)$ . The complex  $A_p B_q C_r$  will be referred to as the  $(p, q, r)$  species or complex.

In the formation of the different two and three component complexes in the present system protons are split off and consequently  $p$  will obtain negative values.

Accurate equilibrium data for  $\text{H}^+ - \text{Ge}(\text{OH})_4$  (25°C and 0.5 m NaCl) have already been presented by Ingri.<sup>10</sup> He reports the following species and formation constants (given on the molal scale):



Note that the values of the constants given by Ingri are calculated with  $\text{OH}^-$  as component and they have been recalculated with  $\text{H}^+$  as component using the ionic product of water in 0.5 m NaCl medium ( $\log K_w = -13.70$ ).<sup>13,14</sup> The equilibrium constants in the 0.5 M NaCl medium are assumed to have the same values as in the 0.5 m NaCl medium.

We have found that within the pH-range  $1 < \text{pH} < 9$  mannitol does not react either with  $\text{H}^+$  or  $\text{OH}^-$ .

Applying the law of mass action to equilibria (3) and (4) the conditions for the concentrations give:

$$B = b + B_1 + \sum q \beta_{pq} h^p b^q c^r \quad (5)$$

$$C = c + \sum r \beta_{pqr} h^p b^q c^r \quad (6)$$

$$H = h + B_1 Z_1 + \sum p \beta_{pqr} h^p b^q c^r \quad (7)$$

where  $b = [\text{Ge}(\text{OH})_4]$ ,  $c = [\text{C}_6\text{H}_{14}\text{O}_6]$ ,  $h = [\text{H}^+]$ ,  $\beta_{pqr} = [A_p B_q C_r] h^{-p} b^{-q} c^{-r}$  and  $B_1, B_1 Z_1$  are the "known" quantities for the binary equilibria:

$$B_1 = \beta_{-1,1} h^{-1} b + \beta_{-2,1} h^{-2} b + 8 \beta_{-3,8} h^{-3} b^8 \quad (8)$$

$$B_1 Z_1 = -\beta_{-1,1} h^{-1} b - 2\beta_{-2,1} h^{-2} b - 3 \beta_{-3,8} h^{-3} b^8 \quad (9)$$

The summations are made over all ternary species present.

*Data treatment.* The refinement of constants and error calculations have been made with the least squares program LETAGROPVRID,<sup>15</sup> version ETITR.<sup>16</sup> The error squares sums  $U = \sum (H_{\text{calc}} - H)^2$  or  $U = \sum (Z_{\text{calc}} - Z)^2$  have been minimized. The standard deviations are defined and calculated according to Sillén.<sup>17,18</sup> The computation has been performed both on CD 3600 (Uppsala) and on CD 3200 (Umeå).

## DATA, CALCULATIONS AND RESULTS

In Fig. 1 we have plotted experimental data  $Z(\log h)_{BC}$  for a section at  $B = 2.5 \text{ mM}$  and with  $C = 5, 10, 20, 40, 80, 160,$  and  $320 \text{ mM}$ .

Similar diagrams were obtained also for the other  $B$  sections studied  $B(C)$  in mM: 5 (40, 80, 160, 320); 10 (5, 20, 80, 160, 320); 20 (5, 20, 80, 160, 320); 30 (80, 320) but for clarity these data have been omitted in the figure.

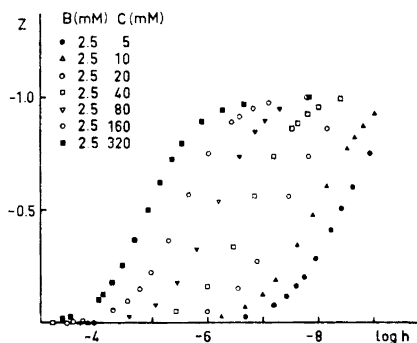


Fig. 1. Experimental data  $Z(\log h)_{BC}$  for a section at  $B=2.5$  mM.

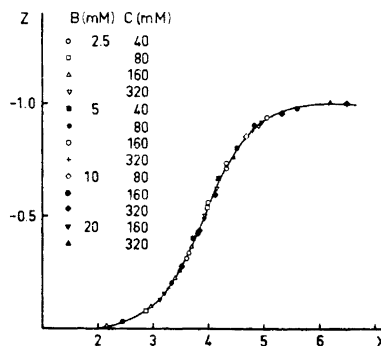


Fig. 2. Experimental data  $Z(X)_{BC}$  for  $C/B \geq 8$ .  $X = -\log h + 2 \log [C + 2(H - h)]$ .

From Fig. 1 we see that in the  $Z$ -range  $-1 < Z < 0$  different curves are obtained for different  $C$ -concentrations, thus clearly indicating that at least one mixed complex  $A_p B_q C_r$  must be formed. The curves seem to reach a limiting value at  $Z = -1$  indicating formation of complexes where one proton has been set free per complexed germanic acid ( $q = -p$ ). Furthermore, for  $C/B > 4$  the space between the curves is approximately constant and the quotients  $(\Delta \log h / \Delta \log C)_{B,Z}$  are equal to two. This would indicate formation of a main complex with  $r/p = -2$  and the simplest complex would be  $A_{-1}BC_2$ . In order to test this proposition further we constructed a diagram  $Z$  versus  $X$ , where  $X = -\log h + 2 \log [C + 2(H - h)]$ .

If the hypothesis of a single complex  $A_{-1}BC_2$  is correct, the plot,  $Z(X)_{BC}$ , would give a single curve independent of  $B$  and  $C$ . This has also been found for  $C/B > 8$  (see Fig. 2), and the plot strongly confirms the complex  $A_{-1}BC_2$  when an excess of mannitol is used. We also determined the formation constant and found  $\log \beta_{-1,1,2} = -3.93 \pm 0.02$ .

For the refinement of the graphically found  $\beta_{-1,1,2}$ -value the LETAGROP computer program was used. The calculation was started with the sections  $B = 2.5$  and  $5.0$  mM.

For  $C/B > 8$  the fit was rather good but for lower ratios systematic deviations were found indicating at least one additional complex. We found that addition of the complex  $(-1, 1, 1)$  completely explained the data.

The calculations were then extended by including the other  $B$ -sections studied ( $B = 10, 20,$  and  $30$  mM). We found that the value of  $\log \beta_{-1,1,1}$  changed (from  $-6.40$  to  $-6.32$ ) and we obtained small systematic deviations which were most marked for  $C/B < 4$ . These deviations could, however, be satisfactorily explained when adding the complex  $(-2, 2, 2)$ .

In order to test the influence of the dissociation constant of  $\text{Ge}(\text{OH})_4$  ( $\beta_{-1,1,0}$ ), a final covariation of  $\beta_{-1,1,0}$ ,  $\beta_{-1,1,2}$ ,  $\beta_{-1,1,1}$ , and  $\beta_{-2,2,2}$  was made which resulted in very small changes in the values of the constants (see Table 2).

Results from the different LETAGROP calculations are collected in Table 2. Data used and residuals  $\Delta = (Z_{\text{calc}} - Z) \times 1000$  obtained for the "best" explanation are collected in Table 1.

Table 1. Experimental data  $H(\log h)_{BC}$ . For each point the quantities  $H$  (in mM),  $\log h$ , and  $\Delta$  are given. The quantity  $\Delta$  is the residual  $(Z_{\text{calc}} - Z) \times 1000$ .

<b>SATS 1</b> B = 0.0025 C = 0.005 .39 -3.411 .11 .30 -3.521 .32 .70 -3.697 .11 .11 -3.940 .01 -0.00 -6.681 -0.57 -0.19 -7.205 -2.24 -0.29 -7.425 -3.32 -0.40 -7.607 -4.49 -0.50 -7.741 -5.92 -0.70 -7.957 -6.55 -1.02 -8.234 -8.54 -1.26 -8.422 2.41 -1.51 -8.616 4.38 -1.88 -8.927 11.73	<b>SATS 6</b> B = 0.0025 C = 0.160 .25 -3.578 -3.69 .20 -3.658 -3.58 .15 -3.753 -4.01 -0.00 -4.300 -2.12 -0.21 -4.557 -1.54 -0.36 -4.784 -1.51 -0.55 -4.994 -1.26 -0.90 -5.298 -2.59 -1.41 -5.663 -2.90 -1.88 -6.018 3.90 -2.23 -6.441 4.84 -2.29 -6.583 7.4 -2.38 -6.821 1.52 -2.44 -7.114 2.04 -2.50 -7.800 5.41	-0.57 -4.119 -2.63 -0.84 -4.276 -1.85 -1.70 -4.665 -2.89 -2.64 -5.000 -2.55 -4.38 -5.798 2.53 -4.77 -6.231 4.84	<b>SATS 12</b> B = 0.010 C = 0.005 4.29 -2.367 -0.03 2.73 -2.564 .02 1.11 -2.963 -1.76 -0.13 -4.492 -2.62 -0.71 -7.282 -5.96 -1.61 -7.779 -8.96 -2.11 -7.975 -10.96 -2.91 -8.221 -11.32 -3.65 -8.413 -8.66 -4.67 -8.602 -3.82 -5.23 -8.766 1.55 -6.15 -8.956 9.08	<b>SATS 16</b> B = 0.010 C = 0.320 4.85 -2.314 -2.87 2.85 -2.541 -1.32 1.11 -2.927 -2.01 .06 -3.441 -1.52 -0.52 -3.798 -2.03 -1.61 -4.243 -1.08 -2.60 -4.503 -2.54 -4.34 -4.850 -5.01 -5.35 -5.032 -5.85 -5.93 -5.139 -6.50 -6.99 -5.251 -7.44 -7.93 -5.378 -7.73 -8.77 -5.462 -7.19 -9.53 -6.352 -6.24 -9.95 -7.528 -2.60	.87 -3.046 -1.66 -0.34 -3.933 -1.57 -1.49 -4.468 -1.08 -3.12 -4.833 -0.95 -4.11 -5.027 -1.01 -6.50 -5.285 -1.20 -8.22 -5.465 -1.72 -9.79 -5.623 -1.75 -11.25 -5.767 -1.85 -13.74 -5.973 -1.47 -16.89 -6.457 .16 -18.33 -6.774 .64 -19.14 -7.078 1.21 -19.98 -7.948 4.05
<b>SATS 2</b> B = 0.0025 C = 0.010 .36 -3.453 -2.78 .30 -3.528 -0.02 .22 -3.656 -0.48 .15 -3.817 -0.34 .10 -3.983 .27 -0.07 -6.250 .67 -0.17 -6.684 -0.99 -0.31 -6.992 -0.48 -0.47 -7.230 5.35 -0.86 -7.616 -2.35 -1.19 -7.898 -3.02 -1.51 -8.153 -1.39 -1.93 -8.525 4.31 -2.05 -8.859 10.77 -2.18 -8.811 10.77	<b>SATS 7</b> B = 0.0025 C = 0.320 .35 -3.399 -9.07 .29 -3.460 -9.16 .23 -3.531 -10.73 -0.16 -4.036 -10.28 -0.24 -4.118 -7.20 -0.39 -4.276 -3.94 -0.60 -4.445 .23 -0.79 -4.692 4.68 -1.24 -4.925 6.29 -1.55 -5.148 3.92 -1.81 -5.359 1.64 -1.98 -5.537 -2.64 -2.23 -5.902 -6.94 -2.36 -6.265 -10.81 -2.42 -6.661 -12.67 -2.48 -7.839 -5.86	<b>SATS 13</b> B = 0.010 C = 0.020 4.86 -2.314 -0.57 3.62 -2.441 -0.09 1.22 -2.923 -2.24 -0.33 -5.869 -3.18 -0.80 -6.295 -4.28 -1.26 -6.541 -4.86 -2.11 -6.872 -5.40 -2.91 -7.115 -5.05 -3.29 -7.220 -4.95 -4.00 -7.409 -4.31 -4.98 -7.659 -3.76 -5.87 -7.897 -4.08 -6.94 -8.172 -3.89 -7.89 -8.457 -3.17 -8.93 -8.862 .28	<b>SATS 17</b> B = 0.020 C = 0.005 4.90 -2.305 2.86 4.41 -2.445 1.86 2.14 -2.674 -1.21 1.29 -2.909 -2.70 .46 -3.414 -3.70 -0.73 -6.967 -4.30 -2.23 -7.506 -8.07 -3.48 -7.768 -8.31 -5.43 -8.141 -7.49 -7.23 -8.458 -3.18 -8.89 -8.721 4.93 -10.42 -8.937 15.08	<b>SATS 18</b> B = 0.020 C = 0.020 5.31 -2.278 -2.05 3.59 -2.444 .14 1.96 -2.700 1.58 .41 -3.245 1.86 -0.58 -5.748 2.26 -1.77 -6.381 .90 -3.14 -6.770 1.03 -4.45 -7.060 1.15 -6.30 -7.412 .41 -8.03 -7.709 -1.47 -9.66 -7.972 -6.15 -11.67 -8.284 -6.26 -13.08 -8.496 -5.96 -14.41 -8.693 -3.57 -15.66 -8.895 -0.34 -16.46 -9.014 2.63	<b>SATS 21</b> B = 0.020 C = 0.320 6.37 -2.195 -1.04 4.16 -2.377 -0.91 2.78 -2.547 -1.25 1.74 -2.659 -1.19 -0.36 -3.493 -0.94 -2.61 -4.134 -0.05 -4.16 -4.378 -0.33 -5.13 -4.501 -0.52 -6.96 -4.699 -1.19 -8.69 -4.863 .62 -10.18 -5.008 -2.88 -11.61 -5.142 -3.57 -13.25 -5.304 -3.53 -15.23 -5.527 -3.70 -17.31 -5.844 -2.68 -19.46 -6.254 -1.22 -19.99 -7.415 2.34
<b>SATS 3</b> B = 0.0025 C = 0.020 .52 -3.262 -0.11 .46 -3.338 -0.36 .40 -3.401 -0.07 .33 -3.477 -0.68 -0.12 -6.005 -0.12 -0.37 -6.551 -2.02 -0.67 -6.890 -1.96 -1.39 -7.465 -0.97 -1.86 -7.824 11.29 -2.15 -8.163 15.19	<b>SATS 8</b> B = 0.005 C = 0.040 .39 -3.613 -0.49 .31 -3.506 -0.57 .21 -3.673 -0.89 -0.50 -5.781 -2.13 -2.00 -6.610 -0.83 -3.33 -7.126 8.83 -4.02 -7.445 13.53	<b>SATS 14</b> B = 0.010 C = 0.080 4.85 -2.310 4.40 3.23 -2.490 .70 1.78 -2.754 -1.83 .47 -3.348 -3.92 -0.13 -4.454 -4.01 -0.71 -5.051 -4.12 -1.78 -5.509 -4.61 -2.75 -5.771 -4.60 -3.21 -5.875 -4.52 -4.47 -6.136 -5.33 -5.58 -6.356 -5.15 -6.58 -6.562 -4.92 -7.47 -6.771 -4.75 -8.53 -7.094 -4.64 -9.65 -7.616 -4.47 -9.72 -7.947 -3.62	<b>SATS 19</b> B = 0.020 C = 0.080 6.51 -2.184 1.26 4.16 -2.381 -0.54 3.59 -2.445 -0.05 3.04 -2.519 -0.90 -0.09 -4.138 -2.19 -1.30 -5.006 -1.56 -3.37 -5.502 -0.79 -5.29 -5.793 -0.02 -7.09 -6.016 1.20 -8.77 -6.208 2.32 -10.35 -6.383 3.52 -11.83 -6.550 5.06 -13.23 -6.715 6.10 -14.97 -6.942 7.31 -16.19 -7.129 7.65 -18.09 -7.526 6.22 -19.50 -8.145 4.00	<b>SATS 23</b> B = 0.030 C = 0.080 5.63 -2.254 -1.90 3.48 -2.456 .134 2.14 -2.659 1.43 .26 -3.419 2.19 -0.34 -4.183 2.29 -2.04 -5.018 1.62 -4.63 -5.475 1.86 -7.37 -5.792 2.40 -9.79 -6.021 3.77 -12.59 -6.264 6.40 -15.57 -6.513 10.22 -18.54 -6.765 14.96 -21.56 -7.050 17.51 -23.93 -7.306 18.61 -25.77 -7.549 17.92 -27.64 -7.881 15.18 -29.98 -8.885 11.35	
<b>SATS 4</b> B = 0.0025 C = 0.040 .85 -3.070 .47 .75 -3.123 1.65 .60 -3.223 -0.41 .49 -3.314 -1.03 -0.12 -5.443 -2.77 -0.39 -5.998 -1.75 -0.84 -6.437 .95 -1.40 -6.851 6.86 -1.84 -7.195 10.86 -2.15 -7.523 15.03 -2.21 -7.631 10.61 -2.31 -7.813 11.33 -2.38 -8.009 11.27 -2.48 -8.412 15.88	<b>SATS 9</b> B = 0.005 C = 0.080 .42 -3.379 -1.86 .37 -3.435 -2.21 .32 -3.497 -2.40 .27 -3.570 -2.66 -0.12 -4.642 -2.36 -1.00 -5.546 -1.96 -2.00 -5.991 -2.21 -3.12 -6.407 .85 -4.00 -6.786 7.81 -4.50 -7.117 11.04	<b>SATS 15</b> B = 0.010 C = 0.160 4.66 -2.313 -0.02 2.85 -2.545 -1.32 1.66 -2.776 -0.72 .37 -3.370 -1.14 -0.23 -4.055 -0.48 -0.80 -4.693 .37 -1.78 -4.890 -1.10 -2.76 -5.144 -1.91 -3.65 -5.334 -2.94 -4.20 -5.441 -3.35 -5.23 -5.633 -4.14 -6.15 -5.809 -5.03 -7.19 -6.027 -5.37 -8.11 -6.266 -5.39 -9.01 -6.612 -4.90 -9.74 -7.283 -3.61	<b>SATS 20</b> B = 0.020 C = 0.160 6.39 -2.194 -0.09 4.69 -2.311 -0.71 2.80 -2.553 -0.99	<b>SATS 25</b> B = 0.025 C = 0.080 .27 -3.572 -2.91 .23 -3.636 -3.14 .19 -3.714 -3.99 -0.04 -4.591 -3.38 -0.19 -5.065 -1.77 -0.44 -5.460 -0.22 -0.81 -5.810 4.94 -1.34 -6.199 7.61 -1.84 -6.579 11.24 -2.11 -6.862 12.93 -2.24 -7.037 14.88 -2.37 -7.299 16.82	

Table 2. Results from LETAGROP calculations minimizing  $U = \sum (Z_{\text{calc}} - Z)^2$  using data given in Table 1. The value of  $\log \beta_{-3,3,0} = -11.96$  was not varied and  $\log \beta_{-1,1,0}$  was varied only in the two cases when  $3\sigma$  is given.

B (mM)	Number of points	$U \times 10^4$	$\sigma(Z)$	$\log(\beta_{-1,1,0} \pm 3\sigma)$	$\log(\beta_{-1,1,2} \pm 3\sigma)$	$\log(\beta_{-1,1,1} \pm 3\sigma)$	$\log(\beta_{-2,2,2} \pm 3\sigma)$
2.5 and 5.0 ( $C/B \geq 8$ )	102	118	0.0108	-9.03	-3.917 ± 0.011	-	-
2.5 and 5.0 (all ratios)	131	767	0.0243	-9.03	-3.892 ± 0.022	-	-
	»	49	0.0062	-9.03	-3.941 ± 0.007	-6.397 ± 0.035	-
2.5 ≤ B ≤ 30	319	202	0.0080	-9.03	-3.950 ± 0.006	-6.320 ± 0.026	-
»	»	202	0.0080	-9.034 ± 0.037	-3.950 ± 0.006	-6.317 ± 0.039	-
»	»	101	0.0057	-9.03	-3.944 ± 0.004	-6.460 ± 0.038	-10.68 ± 0.09
»	»	90	0.0053	-9.084 ± 0.027	-3.945 ± 0.004	-6.428 ± 0.037	-10.62 ± 0.08

In order to test the existence of uncharged complexes between germanic acid and mannitol we measured the optical rotation of acid solutions ( $\text{pH} \approx 2$ ). For  $B < 30$  mM we found that the optical rotation was the same as for pure mannitol at the corresponding concentration. However, for  $B > 30$  mM there was a small increase in the optical activity, thus indicating the possibility of uncharged complexes.

## CONCLUSIONS

The present investigation has shown that in the system  $\text{H}^+\text{-Ge(OH)}_4\text{-mannitol}$  the main ternary complexes are  $(-1,1,2)$  and  $(-1,1,1)$ . For germanium concentrations greater than 5 mM with not too high mannitol excess additional complexes are indicated. The data range available favouring the formation of these additional complexes is, however, too limited to allow a meaningful data analysis (testing different  $pqr$ -sets). Neither can the concentration range be extended over the entire pH-range studied because of the limited solubility of  $\text{Ge(OH)}_4$  ( $\sim 40$  mM in 0.5 M NaCl). However, some different  $pqr$ -sets were tested and the complex  $(-2,2,2)$  gives a satisfactorily explanation of additional effects.

In all the three ternary complexes one proton is set free per complexed germanic acid ( $p/q = -1$ ). However, for some  $BC$ -combinations we found  $Z$ -values  $< -1$  (indicating complexes with  $p/q < -1$ ) but the corresponding pH-values were  $\gtrsim 9$ . In this pH-range the glass electrode does not give reliable values and to be able to determine these complexes the pH-range must be extended by, for instance, using a hydrogen electrode.

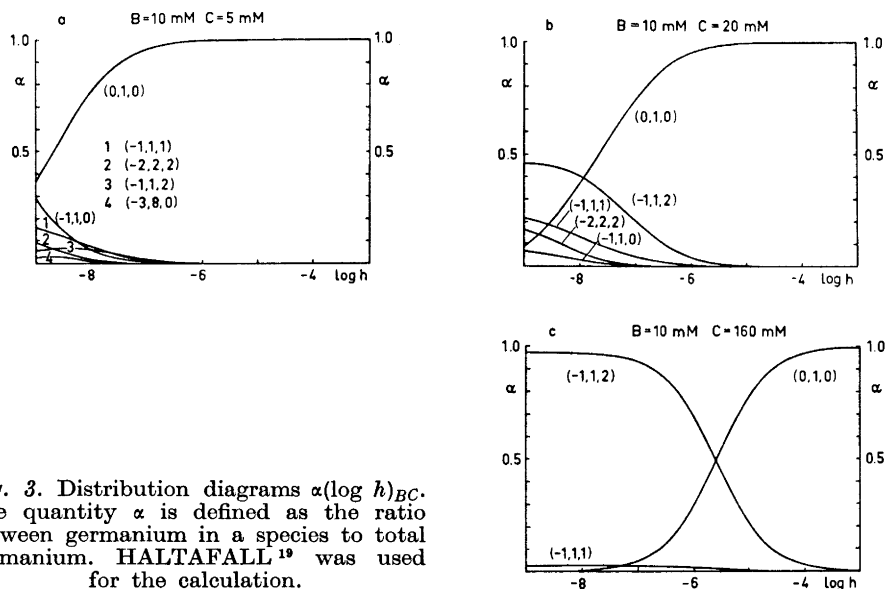


Fig. 3. Distribution diagrams  $\alpha(\log h)_{BC}$ . The quantity  $\alpha$  is defined as the ratio between germanium in a species to total germanium. HALTAFALL<sup>19</sup> was used for the calculation.

Strengths and concentrations of the ternary complexes found in the pH-range 3–9 are illustrated by the distribution diagrams given in Fig. 3, a–c, for  $B, C = 10, 5; 10, 20; 10, 160$  mM, respectively. In Fig. 3, a and b, ( $B/C = 2$  and  $1/2$ ) the  $(-1, 1, 1)$ ,  $(-2, 2, 2)$ , and  $(-1, 1, 2)$  complexes all are present in considerable amounts, but in Fig. 3c, ( $B/C = 1/16$ ), the  $(-1, 1, 2)$ -complex is quite predominating. It is not surprising that investigators using a great excess of mannitol have been able to explain their data with solely the  $(-1, 1, 2)$ -complex.

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