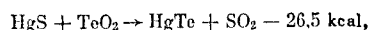


545°, contains ~99% Te and ~0.5% Hg. The results indicate that the first effect is due to the formation of mercury telluride according to the reaction



and that the second effect is due to its decomposition.

This last result agrees with data⁴ on the peritectic decomposition of HgTe at 550°.

The results of heating an equimolar mixture of HgS and TeO₂ at 400–600° (Table 7) show that mercury telluride can be obtained by heating such a mixture in the range 400–500°. The optimal temperature at which the product is HgTe containing the minimal quantity (1.0–1.5%) of impurities is 450°.

SUMMARY

1. The reaction of zinc, cadmium, and mercury sulphides with TeO₂ has been studied by chemical analysis and by thermographic and X-ray diffraction methods. The temperature dependence of the free energy changes for the main reactions assumed to be possible when the metal sulphides are heated with TeO₂ has been calculated. Agreement is observed between the calculated and experimental data.
2. The chief processes taking place when ZnS is heated with TeO₂ at 400–700° involve the oxidation of zinc sulphide, so that this method is unsuitable for the preparation of zinc telluride.
3. Despite the analogy in the primary reactions of CdS and ZnS with TeO₂ (oxidation of the sulphides to MO and MSO₄), the final product obtained by heating an equimolar mixture of CdS and TeO₂ is almost pure CdTe. The formation of CdTe takes place by secondary reactions.
4. The formation of HgTe by the reaction of HgS with TeO₂ is not complicated to any significant extent by side reactions.
5. The reaction between MS and TeO₂ can be used in practice to prepare cadmium and mercury tellurides.

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HYDROXO-COMPLEXES OF GERMANIUM(IV)

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Complex formation by germanium with hydroxide ions has been little studied, and the available information is incomplete and contradictory. De Carvalho and Lederer¹ state that germanium cations may exist in acid solutions. Everest and Salmon², on the basis of ion-exchange data, deny that formation of cationic forms of germanium is possible in the pH range 7–1. In electromigration experiments, however, germanium cations were detected at pH ~ 7, the quantity increasing with decrease in pH. These results were confirmed by experiments on the sorption of germanium by ion-exchange resins under dynamic⁴ and static⁵ conditions. Kovalenko and Reznik⁶ studied germanium hydroxide, but it was shown^{7–9} that their results cannot yet be accepted. The existence of highly charged germanium cations in strongly acidic solutions has been assumed and confirmed by the formation of germanium disulphide GeS₂ and dihydroxogermanium hexacyanoferrate(II) [Ge(OH)₂]₂[Fe(CN)₆] in 4–5 N HCl.¹⁰ After comparing the solubilities of GeO₂ and As₂O₃ in hydrochloric acid, Pugh¹¹ suggests that the basic dissociation constant for germanium dioxide should be less than 1 × 10⁻¹⁴.

There are no other quantitative data on the formation of cationic forms of germanium, and the existence of many reactions which undoubtedly involve germanium cations makes it necessary to obtain such data.

Procedure

To obtain data for calculating the constants characterising complex formation by germanium with hydroxide ions, we extracted germanium tetrachloride from hydrochloric acid solutions using carbon tetrachloride. The calculations were based on the relationships given by Fomin and Maierova¹² and Fronaeus^{13,14}.

In the extraction of GeCl₄ with carbon tetrachloride, the equilibrium



is displaced to the right. Germanium tetrachloride is un-ionised and is transferred to the organic phase. Chemical reaction between the solvent and the substance being extracted is not observed here¹⁵. The distribution constant for germanium is

$$K_d = \frac{[\text{GeCl}_4]_o}{c_{\text{org}}} \quad (2)$$

The subscripts o and a refer to the organic and aqueous phases respectively. When the temperature, ionic strength, and Cl⁻ ion concentration are constant, the extraction constant

$$K = \frac{[\text{GeCl}_4]_o}{[\text{Ge}^{4+}]_a [\text{Cl}^-]_a^4} \quad (3)$$

depends only on the concentration of non-hydrolysed Ge⁴⁺ ions.

Almost no extraction of HCl takes place¹⁶. The cumulative constants for the formation of complexes by germanium with hydroxide ions are defined as

$$\beta_i = \frac{[Ge(OH)_i]}{[Ge^{4+}][OH^-]^i} \quad (4)$$

The concentration of germanium in the aqueous solution is then

$$c_{Ge,a} = [Ge^{4+}] \left(1 + \sum \beta_i [OH^-]^i \right) \quad (5)$$

From Eqns. (2), (3), and (5), we obtain:

$$1 + \sum \beta_i [OH^-]^i = K \frac{[Cl^-]^4}{K_d} \quad (6)$$

Replacement of $[Cl^-]^4/K_d$ by S and the necessary transformation give the equation

$$\frac{\bar{n}}{[OH^-]} = \frac{d \ln S}{d [OH^-]} \quad (7)$$

where \bar{n} is the number of hydroxide ions corresponding to one germanium atom, or the formation function¹⁷.

The quantity $\bar{n}/[OH^-]$ is determined as the slope of the tangent at a given point to the curve giving the dependence of $\ln S$ on $[OH^-]$. The values of the constants β_i are found from graphs of the auxiliary functions G_i , on the basis of the relationships

$$\lim_{[OH^-] \rightarrow 0} G_1 = \lim_{[OH^-] \rightarrow 0} \frac{\bar{n}}{[OH^-]} = \beta_1 \quad (8)$$

$$\lim_{[OH^-] \rightarrow 0} G_2 = \lim_{[OH^-] \rightarrow 0} \frac{G_1 - \beta_1}{[OH^-]} = 2\beta_2 - \beta_1^2 \quad (9)$$

$$\lim_{[OH^-] \rightarrow 0} G_3 = \lim_{[OH^-] \rightarrow 0} \frac{G_2 - (2\beta_2 - \beta_1^2)}{[OH^-]} = 3\beta_3 - 3\beta_1\beta_2 + \beta_1^3 \quad (10)$$

$$\lim_{[OH^-] \rightarrow 0} G_4 = \lim_{[OH^-] \rightarrow 0} \frac{G_3 - (3\beta_3 - 3\beta_1\beta_2 + \beta_1^3)}{[OH^-]} = 4\beta_4 - 4\beta_1\beta_2 + 4\beta_1^2\beta_2 - 2\beta_1^3 - \beta_1^4 \quad (11)$$

According to Fronaeus, if we have the function

$$X([OH^-]) = 1 + \sum \beta_i [OH^-]^i \quad (12)$$

then

$$\ln X([OH^-]) = \int_0^{[OH^-]} \frac{\bar{n}}{[OH^-]} d[OH^-] \quad (13)$$

The values of $X([OH^-])$ are found from the graph giving the dependence of $\bar{n}/[OH^-]$ on $[OH^-]$ and the values of β_i are determined using the relationships

$$\lim_{[OH^-] \rightarrow 0} Y([OH^-]) = \lim_{[OH^-] \rightarrow 0} \frac{X([OH^-]) - 1}{[OH^-]} = \beta_1 \quad (14)$$

$$\lim_{[OH^-] \rightarrow 0} Z([OH^-]) = \lim_{[OH^-] \rightarrow 0} \frac{Y([OH^-]) - \beta_1}{[OH^-]} = \beta_2 \quad (15)$$

$$\lim_{[OH^-] \rightarrow 0} U([OH^-]) = \lim_{[OH^-] \rightarrow 0} \frac{Z([OH^-]) - \beta_2}{[OH^-]} = \beta_3 \quad (16)$$

$$\lim_{[OH^-] \rightarrow 0} V([OH^-]) = \lim_{[OH^-] \rightarrow 0} \frac{U([OH^-]) - \beta_3}{[OH^-]} = \beta_4 \quad (17)$$

EXPERIMENTAL

We used highly pure germanium dioxide containing not more than $1 \times 10^{-5}\%$ impurities; carbon tetrachloride purified by distillation; "chemically pure" or "analytical reagent" grades of hydrochloric acid, sodium hydroxide,

and lithium chloride; and water which had been deionised using ion-exchangers.

The extraction was carried out in separating funnels from solutions containing 5×10^{-3} M GeO_2 ; this excluded the possibility of formation of polymeric forms of germanium¹⁸. The concentrations of the metal in the aqueous and organic (after re-extraction with water) phases were determined by the photometric phenylfluorone method¹⁹. The concentration of Cl^- ions in the experiments was equal to 8. This made it possible to study the extraction of germanium tetrachloride over a fairly wide range of HCl concentrations from 0.2 N to 5 N. To keep the ionic strength constant as the hydrochloric acid concentration was varied, we used a lithium chloride solution whose Cl^- concentration was determined by Mohr's method. The phase volumes were 10 ml and remained almost unchanged during extraction. The duration of extraction (1 min) was sufficient for equilibrium to be reached. The concentration of hydrochloric acid in the aqueous phase was determined by titrating with 0.1 N or 0.2 N alkali solution. The experiments were carried out at $25 \pm 0.5^\circ$. The ionic product of water at 25° was taken as 1.27×10^{-14} .²⁰

RESULTS

The original data for construction of the graphical relationships are given in Tables 1-3. The values of β_i , determined by extrapolation from the graphs of the auxiliary functions by the method of Fomin and Maiorova, are $\beta_1 = 6.0 \times 10^{14}$, $\beta_2 = 1.5 \times 10^{29}$, $\beta_3 = 1.9 \times 10^{43}$, and $\beta_4 = 1.1 \times 10^{57}$, and the values obtained by Fronaeus' method

TABLE 1. Extraction of germanium from hydrochloric acid solutions using carbon tetrachloride (phase volumes 10 ml, ionic strength 8, temperature 25°).

$[H^+]$, M	$10^{24}[OH^-]$, M	Quantity of Ge in aqueous phase, mg	Quantity of Ge in organic phase, mg	K_d	$\ln S$
4.960	0.256	0.086	3.060	35.58	4.746
3.936	0.323	0.117	3.080	26.32	5.047
2.996	0.424	0.173	2.775	18.04	5.542
1.970	0.645	0.323	2.780	8.61	6.155
1.570	0.809	0.463	2.875	6.23	6.492
1.287	0.987	0.712	2.875	3.62	7.032
0.970	1.309	1.320	1.919	1.45	7.944
0.782	1.624	1.904	1.705	0.90	8.431
0.592	2.145	2.400	0.913	0.38	9.284
0.400	3.175	2.920	0.370	0.13	10.383
0.303	4.188	3.032	0.232	0.09	10.677
0.264	4.801	3.070	0.223	0.07	10.940
0.214	5.940	3.120	0.174	0.06	11.204
0.197	5.446	3.720	0.213	0.06	11.178

TABLE 2. Calculation of the auxiliary functions for determining the constants β_i by the method of Fomin and Maiorova.

$10^{14}[OH^-]$, M	$10^{24}G_1$	$10^{28}G_2$	$10^{42}G_3$	$10^{56}G_4$	$10^{24}[OH^-]$, M	$10^{14}G_1$	$10^{28}G_2$	$10^{42}G_3$	$10^{56}G_4$
0.33	4.36	-4.96	3.16	-1.34	1.50	2.00	-2.67	2.20	-0.93
0.40	4.00	-4.75	3.12	-1.25	2.00	1.61	-2.25	1.98	-0.85
0.50	3.73	-4.53	3.00	-1.20	2.50	1.00	-1.94	1.58	-0.79
0.55	3.33	-4.45	2.91	-1.18	3.00	0.91	-1.73	1.42	-0.72
0.75	2.92	-4.00	2.73	-1.13	4.00	0.42	-1.40	1.15	-0.61
1.00	2.59	-3.41	2.59	-1.05	5.00	0.25	-1.15	0.97	-0.53
1.25	2.31	-2.95	2.40	-1.00	6.00	0.18	-0.97	0.84	-0.45

TABLE 3. Calculation of the auxiliary functions for determining the constants β_i by Fronaeus' method.

$10^{14}[\text{OH}^-], \text{M}$	$X([\text{OH}^-])$	$10^{28} Y([\text{OH}^-])$	$10^{42} Z([\text{OH}^-])$	$10^{56} U([\text{OH}^-])$	$10^{70} V([\text{OH}^-])$
0.30	4.83	12.77	22.57	25.23	4.10
0.40	7.46	16.16	25.40	26.00	5.00
0.50	11.04	20.08	28.16	26.32	4.64
0.60	15.74	24.57	30.95	26.75	4.58
0.80	29.31	35.39	36.74	27.18	3.98
1.00	53.35	49.35	43.35	28.35	4.35
1.25	92.26	73.01	53.61	31.89	5.52
1.50	167.10	110.73	69.82	35.55	8.37

are 6.0×10^{14} , 1.5×10^{29} , 2.4×10^{43} , and 0.4×10^{57} respectively. The geometric mean values²¹ of the constants β_3 and β_4 are 2.1×10^{43} and 0.7×10^{57} .

Substituting the mean values of the constants, obtained by the two methods, in Eqn. (7), we calculated the values of $\bar{\pi}/[\text{OH}^-]$ and compared these with the values found from the graph in Fig. 2. Table 4 shows that Eqn. (7) is satisfied by the four values obtained for the constants β_i , so that the values of β_5 and β_6 should be very close to or equal to zero; this is confirmed by further calculations. It may thus be assumed that the penta- and hexa-coordinated anionic complexes $[\text{Ge}(\text{OH})_5]^-$ and $[\text{Ge}(\text{OH})_6]^{2-}$ do not exist in acid medium. These anions were detected by Brintzinger²² only in strongly alkaline solutions. The contradictory results obtained in the study of germanium cations in weakly acidic solutions are apparently due to differences in the sensitivity of the methods used. For a solution with an ionic strength of 8 and a germanium concentration less than 0.01 M, in which there is no polymerisation¹⁸, calculation shows that with change in pH from 7 to 1 the quantity of cations increases approximately from $1 \times 10^{-5}\%$ to 19%, relative to the total germanium concentration.

The values of the constants β_i were used to calculate the consecutive formation constants for the complexes formed by germanium with OH^- ions

$$K_i = \frac{[\text{Ge}(\text{OH})_i^{4-i}]}{[\text{Ge}(\text{OH})_{i-1}^{4-(i-1)}][\text{OH}^-]} \quad (18)$$

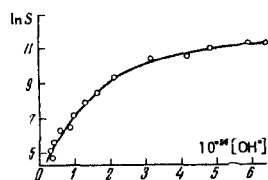
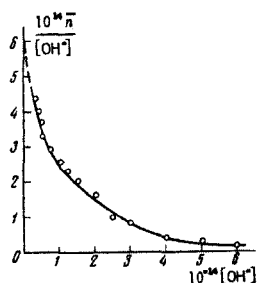
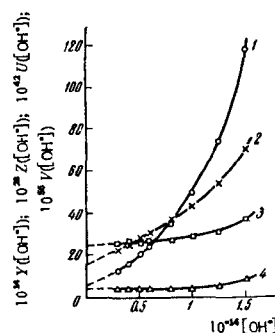
Fig. 1. Dependence of $\ln S$ on $[\text{OH}^-]$.Fig. 2. Determination of β_1 .

Fig. 3. Determination of the constants by Fronaeus' method:

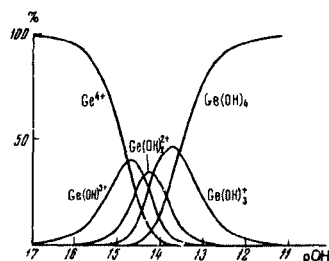
- 1) $10^{14} Y([\text{OH}^-])$; 2) $10^{28} Z([\text{OH}^-])$;
- 3) $10^{42} U([\text{OH}^-])$; 4) $10^{56} V([\text{OH}^-])$.

TABLE 4. Comparison of the calculated and experimental values of $\bar{\pi}/[\text{OH}^-]$.

$10^{14}[\text{OH}^-]$	$\frac{10^{14} \bar{\pi}}{[\text{OH}^-]}$		$10^{14}[\text{OH}^-]$	$\frac{10^{14} \bar{\pi}}{[\text{OH}^-]}$	
	calculated	from graph in Fig. 2		calculated	from graph in Fig. 2
0.30	4.49	4.53	1.00	2.54	2.58
0.40	4.08	4.13	1.25	2.18	2.21
0.50	3.72	3.77	1.50	1.91	1.94
0.80	3.41	3.46	2.00	1.54	1.55
0.90	2.92	2.96			

TABLE 5. Characteristics of the complexes $[\text{Ge}(\text{OH})_i]^{4-i+}$ (ionic strength 8, temperature 25°).

Cumulative formation constants, β_i	Consecutive formation constants, K_i	Hydrolysis constants, K_{hi}	Basic dissociation constants, K_{bi}
$\beta_1 = 6.0 \cdot 10^{14}$	$K_1 = 6.0 \cdot 10^{14}$	$K_{h1} = 7.6$	$K_{b1} = 3.0 \cdot 10^{-14}$
$\beta_2 = 1.5 \cdot 10^{29}$	$K_2 = 2.5 \cdot 10^{14}$	$K_{h2} = 3.2$	$K_{b2} = 7.1 \cdot 10^{-15}$
$\beta_3 = 2.1 \cdot 10^{43}$	$K_3 = 1.4 \cdot 10^{14}$	$K_{h3} = 1.8$	$K_{b3} = 4.0 \cdot 10^{-16}$
$\beta_4 = 7.0 \cdot 10^{56}$	$K_4 = 3.3 \cdot 10^{13}$	$K_{h4} = 0.4$	$K_{b4} = 1.7 \cdot 10^{-15}$

Fig. 4. pOH dependence of the distribution of $[\text{Ge}(\text{OH})_i]^{4-i+}$ complexes.

the hydrolysis constants for the Ge^{4+} ion

$$K_{hi} = \frac{[\text{Ge}(\text{OH})_i^{4-i}][\text{H}^+]}{[\text{Ge}(\text{OH})_{i-1}^{4-(i-1)}][\text{OH}^-]} \quad (19)$$

and the basic dissociation constants of germanium hydroxide

$$K_{bi} = \frac{[\text{Ge}(\text{OH})_{i-1}^{4-(i-1)}][\text{OH}^-]}{[\text{Ge}(\text{OH})_i^{4-i}]} \quad (20)$$

SUMMARY

Complex formation by germanium with hydroxide ions has been studied by extracting germanium tetrachloride with carbon tetrachloride at 25° and an ionic strength of 8. The cumulative formation constants of the complexes $[\text{Ge}(\text{OH})_i]^{(4-2)i}$ have been calculated (6.0×10^{14} , 1.5×10^{20} , 2.1×10^{43} , and 7.0×10^{56}) and used to calculate the pOH dependence of the distribution of germanium between the various forms.

The consecutive formation constants for the complexes formed by germanium with OH^- ions (6.0×10^{14} , 2.5×10^{14} , 1.4×10^{14} , and 3.3×10^{13}), the hydrolysis constants for the Ge^{4+} ion (7.6, 3.2, 1.8, and 0.4), and the basic dissociation constants of germanium hydroxide (3.0×10^{-14} , 7.1×10^{-15} , 4.0×10^{-15} , and 1.7×10^{-15}) have been determined.

HYDROTHERMAL PREPARATION OF SILICATES AND GERMANATES WITH STRUCTURES OF THE GARNET TYPE

B. V. Mill'

The discovery in 1956 of the ferrites (garnets) of the rare-earth elements and yttrium¹ stimulated a large number of studies on the crystal chemistry of garnets. Many new compounds were prepared, containing a wide variety of cations in eightfold, sixfold, and fourfold coordination with respect to oxygen ions. A fairly complete review of various types of garnet and possible substitutions in these structures was made by Geller². The new compounds were usually prepared in the form of ceramics by heating compressed mixtures with the appropriate composition in air or in an inert atmosphere at 1000–1400°. We tried to prepare various types of garnet under hydrothermal conditions.

The present paper deals with the preparation of garnets with general formula $A_3^{\text{II}} B_2^{\text{III}} C_3^{\text{IV}} O_{12}$ where $A = \text{Ca, Cd, or Mn}$; $B = \text{Al, Fe, Cr, Ga, or Sc}$; and $C = \text{Si or Ge}$. These include natural garnets (andradite $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, grossular $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, spessartine $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and uvarovite $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ³), the recently prepared $\text{Cd}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Ga}_2\text{Si}_3\text{O}_{12}$ ⁴ and $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ ⁵ and the germanates prepared by Tauber, corresponding to various combinations of A and B⁶ (only $\text{Mn}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ and $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ were not formed at atmospheric pressure — the latter was obtained hydrothermally⁷).

In the literature on the hydrothermal preparation of natural garnets, the fullest information is that on grossular. Grossular in the presence of quartz is stable above 780° and 1500 atm.⁸ At lower temperatures hydrogrossular $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (3-x)\text{SiO}_2 \cdot 2x\text{H}_2\text{O}$ is formed and at 100–120° the hydrogarnet $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ obtained⁹. Michel-Levy¹⁰ prepared grossular (which apparently contained water) at 500° and 500 atm in the form of crystallites with dimensions reaching 40 μm. He also prepared andradite under the same conditions. The hydrogarnet $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and its solid solutions with andradite are known⁹. Spessartine is not formed with alkaline solvents and is obtained with water in the range 400–700°; the addition of Na_2SiF_6 increases the dimensions of the crystals¹¹. The hydrothermal preparation of uvarovite and $\text{Ca}_3\text{Ga}_2\text{Si}_3\text{O}_{12}$ has been reported⁴ but the conditions of formation were not given. Of the germanates, only $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$, $\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$, and $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ have been prepared hydrothermally at 850° and 1000 atm from stoichiometric mixtures of CaCO_3 , the corresponding sesquioxide, and GeO_2 ⁸.

Most published garnet preparations have been carried out in water as solvent, whereas in natural conditions and in the artificial growth of single crystals an important part is played by dissolved salts, bases, or acids. As a rule, the influence of the composition of the charge and the nature of the solvent on the preparation was not studied, although these two factors should probably markedly influence the formation of the various phases, the range of stability of the garnet, and its yield. Some of these problems are examined in the present work.

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