ON POLYGERMANATE ION (REVIEW AND CRITICAL STUDY)

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SUMMARY.—Studies on the solubility of GeO_2 in alkaline solutions showed that, approximately, 2.5 mol of germanium dioxide were dissolved per mol of NaOH. Also, at the neutralization pH, Capeni found a white precipitate of formula $K_2Ge_5O_{11}$. It was interpreted as a polymerization reaction germanic acid $\rightleftharpoons$ polygermanate + H^+, and, according to the most recent papers it presumes that the polygermanate contains eight Ge atoms.

Aside from kinetic reasons, no salt with a Ge/M ratio equal to 8/3 is known; this ratio is, for monovalent cations, 5/2, 7/3 or 9/4 or, for di- and trivalent ones, 1/1 or 1/2. On the other hand, in the presence of manitol (and other polyhydroxilate alcohols) the solubility of GeO_2 is 0.5 mol per mol of NaOH.

All these experimental facts can be interpreted as the high affinity of germanium for the –OH groups. The a salt of polivalent cations may be, for example, $[MgOH]_2GeO_2(OH)_2$ and the germanium polymers are in fact a germanium complex

$$4\ Ge(OH)_4 + GeO_2(OH)_2^{2-} \rightleftharpoons Ge_5O_{11}aq.^{2-}$$

for which the stability constant, according to the experimental mesurements, is $K_4 = 1.4 \cdot 10^{13}$.

RESUMEN.—Los estudios de la solubilidad del GeO_2 en soluciones alcalinas indican que, aproximadamente se disuelven 2.5 mol de dióxido de germanio por mol de hidróxido añadido. Esto, unido al hecho de la aparición de un precipitado, al que se asigna la fórmula $K_2Ge_5O_{11}$, sugiere la formación de un ion polímero, el ion poligermanato, que contiene, según los trabajos más recientes 8 átomos de germanio.

El hecho, sin embargo, de que sales con esta estequiometría sólo se formen con cationes monovalentes (y que no exista ninguna con 8 átomos de germanio), aparte de razones cinéticas, hace que completemos esta revisión sobre el ion poligermanato explicándolo como la formación de un complejo del ion germanato con el ácido germánico libre.

INTRODUCCION

From the first studies by Tschakiran (1) until the recent review by Baes and Mesmer (2), the existence of polynuclear species of germanate derived from germanic acid was acknowledged, although there was not an unanimous agreement on the number of atoms in germanate; also, although this point now appears to have been totally overcome, there were discussions on whether polymerization reached the germanic acid itself, or was limited to the anionic form. In the beginning, all indications appeared to point to the ion $Ge_5O_{11}^{2-}$, but after meticulous work by Ingri (3) and by Haas et al. (4), the existence of an ion with 8 atoms of Ge appeared inquestionable, and therefore the formula $Ge_8O_{16}(H_2O)_5(OH)_3^{3-}$, was proposed, and was even given as structural formula (3).

The existence of a sodium germanate, insoluble to a pH of 9 approximately, appears to be related to the previous equilibrium

$$\text{germanate} \rightleftharpoons \text{octogermanate}$$

that, according to the bibliography, precedes the precipitation of germanate when an alkaline solution of this element is neutralized. For kinetic reasons, however, it appears that the precipitation of the sodium salt cannot be preceded by the formation of a polymer, which signifies a direct union of the 8 ions in the heart of the solution, without going through at least one other species with a lesser degree of polymerization.

In view of the above, we decided to carry out a critical study of the abundant experimental work that exists, to see whether this data could be interpreted without the need for resorting to the formation of a species with such a high degree of polymerization.

BIBLIOGRAPHICAL REVIEW

The solubility of germanium dioxide in acids and alkalis

Puch (5) first studied the solubility of germanium dioxide (hexagonal form) in solutions of acids and bases. The solubility decreased as the acid concentration increased and, with the acids used by him (sulphuric and hydrochloric), a law for silicate, as enunciated by Lenher and Merrill (6), is accomplished with:

where S is the solubility in mol per 1000 g of water and N the normality of the acid[1], a law which is also found to apply in other oxides such as those of As(V) and B(III).

This decrease in solubility with the increase in acidity is explained by Pugh (op. cit.) who writes *"it is obvious that germanium hydroxide is ionising predominantly as an acid, its ionization, and consequently its solubility, being diminished by the introduction of foreign hydrogen ions"*, considering the the hypothetical: $Ge(OH)_4$ as an acid, rather than a hydroxide.

With the dialysis coefficient which is constant between pH 8.4 and 8.8, they calculated the molecular weight of the corresponding anion, to which they gave a value of 548 (fórmula weight of $Ge_5O_{11}{}^{2-} = 539$). Beginning at pH 8.8, the dialysis coefficient rises again, indicating the existence of a monomeric species. In any case, the authors noted the existence of a precipitate that formed on the membrane and made measurements difficult.

Carpeni and Tchakirian (8), in a note on the electrochemistry of aqueous solutions of germanate dioxide, explained their results as a balance between mono- and pentagermanic acid molecules, which in a medium of 2N of KCl gave rise, at a pH of about 9, to a white precipitate similar to that described by Schwartz and Huf (7).

Alkaline Pentagermanate

In another note, Tchakirian and Carpeni (9), report on the composition and properties of the precipitate they obtained when adding potassium hydroxide up to a pH near 9, to a saturated solution 2N of KC1 of germanate dioxide. The product obtained was washed with bidistilled water and dried, and no chlorides were detected in it. In accordance with the electrometric titration, they concluded that its composition must be K_2Ge_5O (11).

Figure 2 gives the solubility graph against the pH, in mmol GeO2/1 instead of g/100 cc, therefore presuming that the salt contains 58.5% Ge.

In later works CARPENI (10) and (11), again stated that the formation of the precipitate, that he called *"polygermanate isohydrique"*, is a consequence of the equilibrium[2].

$$5\,GeO_3H_2 \rightleftarrows Ge_5O_{11}H_2 + 4\,H_2O$$

Suchay (12), using data from the work by Roth and Scharz (14), was however of the opinion that in an aqueous solution GeO_2 is in the form of a monomenic acid and that polymerization is reached as a consequence of the equilibrium that he wrote[3].

$$5\,GeO_3H_2 \rightleftarrows Ge_5O_{11}{}^{2-} + 4\,H_2O + 2\,H^+$$

Everest and Salmond (19) attempted to approach the

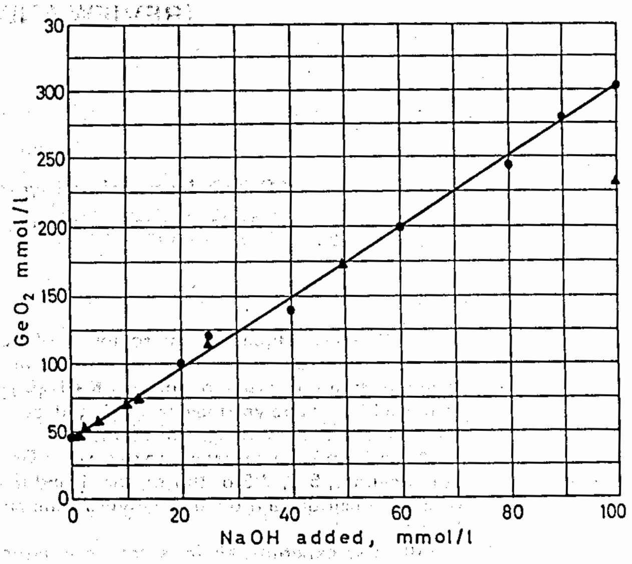

Figure 1

Solubility of GeO_2 in alkaline solution according to the amount of added sodium hidroxide. ● According Pugh (5)
▲ According Lurissen-Teyssedre (20)

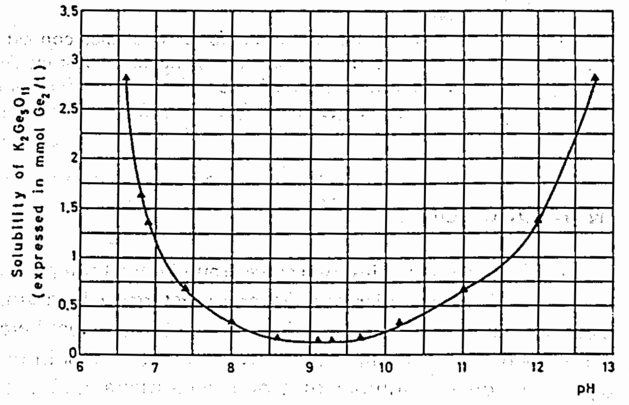

Figure 2

Solubility curve for potassium polygermanate in solution 2N of ClK, according to data taken from Tchakirian and Carpeni (9) (as far as possible, we reproduce the formulae and the symbols of the authors in their original papers).

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[1] In accordance with the experimental values of Pugh (5) the Henher and Merrill equation takes the following values:

For sulphuric acid at 25° C

$\log S\ (mol/l) = 1.3692 - 0.11176\ N$

For hydrochloric acid at 25° C up to N= 5

$\log S = -1.3692 - 0.1541\ N$

[2] Both the che concept of "isohydric point" and the mentioned equilibrium of mono-pentagermanic acids, caused great arguments in their time (see Suchay and Teyssedre (13), Bye (15) and Suchay (12) for example).

[3] Regarding the formula for germanic acid, we have used up to this point the one given by the investigators themselves, who write GeO_3H_2 equivalent to that for carbonic acid, since the fórmula $Ge(OH)_4$ appeared to correspond to a germanic hydroxide. Based on the values for the two ionization constants of germanic acid, Kossiakokk and Harker (16) demonstrated that these are more in accordance with the formula $H_2GeO_4H_2$ than with GeO_3H_2 although, as demonstrated by McGowan (17) and Ricci (18), it is incorrect to try to obtain other conclusions from these measurements, such as those given by Kossiakokk and Harker when referring to the structural formula of the molecule.

problem of polygermanate through another way. After showing that the resin *Amberlite IRA-400* does not sorb germanic acid as a non-dissociated monomer species, they studied the sorption of germanium in competition with the chloride ion within the pH interval from 4 to 13. Starting with a solution of Ge 0.032 m, they found that the maximum sorption took place at a pH of 9.0 – 9.2, with the ratio R (mols of Ge sorbed to resin equivalents) being 2.53.

Lourijsen-Teyssedre (20) reconsidered the tests by Carpeni and Tchakirian (8), repeating the pH= f (x, c) curve, where x is the number of mol of NaOH added by at-g of Ge and c the concentration of Ge in at-g/1. She used solutions of Ge of concentrations between 0.04 and 0.005 at-g/1 in Na_2SO_4, finding the debated isohydric point for a value of x= 0.38. She also repeated Pugh's measurements and both are given in fig. 1.

From the slope of the line (for which she allows the value m= 2.5, attributing the small deviation to experimental errors) she deduced that the pentagermanate ion $Ge_5O_{11}^{2-}$ is formed in the neutralization of the monogermanic acid and later, with more alkali it becomes the monogermanate ion GeO_3H^-. From is experimental values, she calculated (presumably at 25°C) the value of the equilibrium constant K_5 of the reaction.

$$Ge_5O_{11}^{2-} + 4\,H_2O \rightleftarrows 3\,GeO_3H_2 + 2\,GeO_3H^- \quad [1]$$

Combining the equilibrium constant K_5 of reaction [1] with the constant $K_1{}^4$ of the dissociation equilibrium [2]:

$$GeO_3H_2 \rightleftarrows GeO_3H^- + H^+ \quad [2]$$

she obtained

$$4 \log A = \log (K_5/2K^2) + \log B$$

where A and B were respectively algebraic expressions for x, a_{H^+} and K.

For the value of K_1, she considered that the semineutralization pH, when c → 0, is equal to pK. Under these conditions, for a pH = 9.08, she deduced[4] that $K = 8.5 \cdot 10^{-10}$. With the experimental values obtained, and representing log B against log A, she obtained a straight line with an angular coefficient of 4 (the experimental value is 3.96) and an ordinate at origin of — 9.5, from which she deduced a value of $k_5 = 4.55 \cdot 10^{-9}$ which, in accordance with our observations[5], has to be revised.

Alkali hepata- and enneagermanate

Nowotny and Wittmann (21) described the properties and structure of some alkali germanates in a general formula

$$M_3HGe_7O_{16}.4H_2O$$

where M= Li, Na, NH_4, K, Rb, Cs that in a later work (see Wittmann and Nowotny (22)) they expanded to M= = Tl, Ag. In these papers, besides X-ray patterns of the different salts and the crystalographic constants derived from them, they gave the results of thermogravimetric (TGA) and differential thermal (DTA) analyses. In the case of the sodium salt, the TGA shows a loss of 4 molecules of water at around 150°C and the mainder (1/2 molecule) at about 300°C, while the DTA gives an exothermic reaction between 550 and 600°C (which does not appear in the ammonia salt). According to the authors, this could correspond to the formation of the salt $M_2Ge_4O_9$ ($M_4Ge_9O_{20}$?).

Shaw, Corwin and Edward (23) studied the hydrothermal reactions in the system GeO_2-NaOH-H_2O at tempeeratures between 100 and 400°C. The reaction of GeO_2 with water does not give rise to any new crystalline formation[6], while with solutions of sodium hydroxide two forms appear, one at low temperature corresponding to the hepatagermanate described above, and another at higher temperature to which the formula $Na_2Ge_4O_9$ was assigned, although another paper Shaw and Corwin (23) showed that this formula is really $Na_4Ge_9O_{20}$.

Cell dimenions (a_0= 14.985 ± 0.010 Å; C_0= 7.382 ± ± 0,001 Å) and space group ($14_1/a$) where determined from single crystal diffraction data, in a later paper, by White, Shaw and Corwin (26).

Ingri and Lundgren (27) also isolated the compound formed by hydrothermal reaction at 300°C between the crystals in hydrated form obtained at low temperature and its mother liquid; later, the same authors (28) gave the same space group and dimensions of the unit cell. Using three-dimensional Patterson and Fourier methods, the Ge, O, Na positions could be determined.

Heptagermanate ion

In the paper already mentioned, Nowotny and Wittmann (21), starting with the heptagermanate structure, presumed that the ion $GeO_4{}^{4-}$ exists in an aqueous solution with high alkalinity, and the $H_2GeO_4{}^{2-}$ at medium alkalinity, both being monomers, while in a neutral medium a polymer is formed that could have the formula $HGe_7O_{16}.aq^{3-}$ or another analogous formula in with the germanate polymerized in a structure in wich, the germanium atoms are joined through "O-Atom-ionem" (sic), establishing a hydrolysis equilibrium like:

$$m\,H_2GeO_4{}^{2-} + H_2O \rightleftarrows (polymer) + n\,OH^-$$

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[4] While within the value K_5 only concentrations are used, and is really being taken is the quotient for the equilibrium Q_5, in the case of K_1 she mixes concentrations for species and activities for H^+. Since she is working in a medium of ionic strenghtI= = 1/2(0.1×4 + 0.2)= 0.3 a correction can be made
$\log[H^+] = - pH - fH$ where $fH = -0.51 \cdot \sqrt{I}/(1+\sqrt{I}) - 0.21 = 0.12.$

[5] Aside from the fact that for pK = 9.08 we have $K = 8.31 \cdot 10^{-10}$, the currently accepted value for K_1 (see Baes and Mesmer (2)) is $4.90 \cdot 10^{-10}$ which for a value of I = 0,3 would give $Q = 1.08 \cdot 10^{-9}$.

[6] The statement by the author that there are no new crystalline formations from the reaction between GeO_2 and water, should be clarified. It is true that, in the light of present knowledge, it is clear that new substances are not formed (the hypothetical pentagermanic acid, for example). Nevertheless it has also been demonstrated that in an aqueous solution above 185°C it takes place the transformation of the soluble hexagonal variety of GeO_2, which is that normally used in experiments, in the tetragonal insoluble (see, for example, Kuzima, Litin and Kurazh-

that in a later paper (Wittmann and Nowotny (21)) is defined by the following expression

$$7\,H_2GeO_4{}^{2-} \longleftrightarrow H_2O + HGe_7O_{16}{}^{3-} + 11\,OH^-$$

Everest and Harrison (29), on learning that the composition of the precipitate was $M_3HGe_7O_{16}$ instead of $M_2Ge_5O_{11}$ as proposed by Carpeni[7], reviewed the paper of Everest and Salmon (18), justifying the value R= 2.52 on which they based the existence of the pentagermanate ion after having worked with very diluted solutions of germanate. They repeated their sorption tests with resins, using pH 9 solutions with a GeO_2 content of 0.75 to 28 (?) g/l, and found that R goes from 1.8 to 3.5 the latter being the asymptotic value reached beginn at about 16 gr/l. Starting with this value, they deduced that the formula for the polygermanate should be $H_2Ge_7O_{16}{}^{2-}$ as the final step on the equilibrium

$$\text{monogermanate} \longleftrightarrow \text{pentagermanate} \longleftrightarrow \text{heptagermanate}$$

The solution for these tests were prepared by disolving at 100°C, 10 g of GeO_2 finely ground in 100 ml of water, and adding NaOH up to pH 5.8.

Octogermanate Ion

Ingri (3), who had previously identified the crystalline structure of the enneagermanate (27), (28) by electrometric titration, explored the possible species derived from germanic acid. To do so, he employed solutions between 0.04 and 0.005 m of total germanate in a medium 0.5 N of NaCl, since at values equal to or above 0.04 m (see fig. 2) the heptagermanate precipitates, while at values below 0.005 m only the monomeric species $GeO(OH)_3{}^-$ and $GeO_2(OH)_2{}^{2-}$ are detected.

From the measurement of potential by the glass electrode and presuming that the ionic strength of the solution is constant, he established the value for $[H^+]$, while he analytically determined B and H, where B is the total concentration of germanium (IV) and H the analytical excess of concentration of H^+ ions, presuming that all the germanium was $Ge(OH)_4$. Using these three magnitudes, he determined a fourth, Z, representing the average number of OH^- ions joined to the $Ge(OH)_4$.

$$BZ = [H^+] - H + K_w[H^+]$$

where $\log K_w = -13.70$.

After obtaining the experimental values, he passed them through a computer, presuming that the two mononuclear species, there existed a polynuclear species of the A_pB_q type [where A= OH and B= $Ge(OH)_4$]. He then tested the pairs of values for p,q: 2,5 (pentagermanate) and 3,7 (heptagermanate) which were rejected, while the pairs 3,8 and 4,11 (whose quotient is nearer to the experimental value Z= 0.36 ± 0.02) were more acceptable, and of these the pair 3,8 is the most concordant, giving the value $\log \beta_4 = 29.14 \pm 0.05$ for the equilibrium.

$$8\,Ge(OH)_4 + 3\,OH^- \longleftrightarrow [Ge(OH)_4]_8(OH)_3{}^{3-}$$

Haas, Konopik, Mark and Neckel (4), using the same experimental technique and mathematical apparatus as Ingri, confirmed the results of the latter; they used a concentration of total germanium (IV) between 0.00159 and 0.02388 m. Instead of NaCl 0.5 m, they employed two solutions of $NaClO_4$, 0.5 and 1 m, and not only they proved the pairs 2,5 and 3,7, but also the pair 1,2 which corresponds to the species indicated by Antikainen[8], they concluved that the pair best adapted to experimental results, was 3,8.

Baes and Mesmer (2) took the values of Haas et al. extrapolated to zero ionic strength. To do this, they related the equilibrium quotient Q_{xy} to the equilibrium constant k_{xy} of $x\,Ge(OH)_4 + (y-z)\,H_2O \rightleftharpoons Ge_xO_2(OH)^{4-}_{4x+y-2z} + yH^+$ through the formula

$$\log Q_{xy} = \log K_{xy} + a\sqrt{I}/(1+\sqrt{I}) + b\,m_x$$

In Table I we show the corresponding values taken from the mentioned publication.

With these data, Baes and Mesmer have calculated the concentrations of the 4 species in a solution of ionic strength 1 for total concentrations of germanate 0.1 and 10^{-5}. Since the Ingre measurements cover the interval 0.04 to 0.005 m (even though he really only used 0.025 to 0.005 because the polygermanate precipitates at a higher concentration) and those of Haas et al. the interval

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[7] According to a more recent work Carpeni, Hamann, Haladjtan and Perinet (30), the existence of $K_3HGe_7O_{16}$ does not invalidate that of $K_2Ge_5O_{11}$ discovered by Tchakirian and Carpeni. According to Carpeni et al., crystalline heptagermanate, is formed in the alkaline medium acidulating the germanate solution, while the amorphous pentagermanate, is obtained by alkalinizing a solution of germanium dioxide up to pH 9. The pentagermanate, according to these authors, is transformed into the heptagermanate in the course of time or by alkalinizing the solution.

[8] The work by Antikainen (31) to which Haas et al. refers, studies the formation of polynuclear species, using ionic exchange resins. To do this, he proceeds in the following manner: He prepares a solution 0.4-0.5 M of sodium germanate that passes through a resin bed of Amberlite IR-120 (a resin that changes the H^+); naturally after some time the eluate begins to cloud, giving rise to a precipitate. After 2 weeks, he shows that the solution is clear and its germanium content is 0.235 M. Using cryoscopy and potentiometry, he determines in this solution the existence of two anionic polyinucleate sspecies that the calls $Ge_2{}^-$ and $Ge_3{}^-$ giving the following values for the equilibrium constants at 20°C

$$\frac{[H^+][Ge_2{}^-]}{[GeO_3H_2]^2} = 5\cdot10^{-5} \qquad \frac{[Ge_2{}^-]}{[GeO_3H_2][GeO_3H^-]} = 1.9\cdot10^{4}$$

$$\frac{[H^+][Ge_3{}^-]}{[GeO_3H_2]^3} = 2.3\cdot10^{-4} \qquad \frac{[Ge_3{}^-]}{[GeO_3H_2]^2[GeO_3H^-]} = 8.8\cdot10^{4}$$

(these figures presume value of $pK_1 = 8.58$ which differs from that currently accepted 9.31).

TABLE I

Hydrolisis constans of $Ge(OH)_4$, according to Baes and Mesmer (2)

Species	x,y	log $K_{x,y}$	a	b	σ (log Q)
$GeO(OH)_3^-$	1,1	−9.31	1.022	−0.2	± 0.02
$GeO_2(OH)_2^{2-}$	1,2	−21.9	3.066	−0.4	± 0.1
Ge_8O_{16} $(H_2O)_5(OH)_3^{3-}$	8,3	−14.24	6.132	+0.2	± 0.06
GeO2(tetr.) P_s		−4.3	0.000	0.0	± 0.02

TABLE II

Percentages of $[Ge(IV)]$ as $Ge_8O_{16}(H_2O)_5(OH)_3{}^{3-}$ for $I = 0.5\ m$

[*Calculated with data from Baes and Mesmer (2)*]

pH	Ge(IV) concentration, m			
	0.025	0.015	0.005	0.0015
8.0	45.57	22.21	0.075	0.0000
8.1	48.20	25.28	0.118	0.0000
8.2	50.45	28.01	0.175	0.0000
8.3	52.29	30.32	0.245	0.0001
8.4	53.72	32.13	0.318	0.0001
8.5	54.70	33.40	0.383	0.0001
8.6	55.22	34.08	0.422	0.0001
8.7	55.24	34.11	0.425	0.0001
8.8	54.75	33.47	0.387	0.0001
8.9	53.71	32.12	0.318	0.0001
9.0	52.08	30.05	0.235	0.0001
9.1	49.82	27.24	0.157	0.0000
9.2	46.90	23.74	0.094	0.0000

0.02388 to 0.00159 m, we have repeated the calculation[9] for four concentrations (0.025, 0.015, 0.005 and 0.0015 m) with an ionic strength of 0.5 and a temperature of 25°C.

Instead of the corresponding graphs Table II incluves the numerical values of the percentage of the polynuclear species in the pH interval in which maximum concentration occurs.

Germanates of di- and trivalent cations

Germanium was isolated for the first time by Winkel (32) by precipitation with hydrogen sulphide in a strongly acid solution. This analytical method was used for quite a long time as the only available technique, until Muller (33) proposed the determination of Ge as orthoermanate of magnesium, Mg_2GeO_4.

With going neither into details on the analytical precision of the method (the difference between the GeO_2 taken and found is in the order of 0,1%), nor details of the technique used, we shall simply set out below the data related to this study.

The composition is obtained by mixing a solution of < 0.04 M of GeO_2 with two solutions 2 N of $MgSO_4$ and $(NH_4)_2SO_4$, to which a solution of concentrated ammonium hydroxide is added. Before precipitation the soluttion contained

Ge(IV)	0.025 mol/l.
Mg^{2+}	0.156 mol/l.
NH_4^+	0.0937 mol/l.

For precipitation 1.75 mol/l of NH_3 is added.

After ignition to constant weight, the compound has 56,47% of GeO_2 and 43.42% of MgO; values that are very near to the theoretical values of 56.45% and 43.55% for a salt of the formula Mg_2GeO_4 as proposed by the author.

We do not know of any study of the structure of the salts of di and trivalent cations obtained by wet methods (the papers refer to salts obtained by the fusion of the mixture of oxides). However, from the stequiometry of the salts a possible formula might be suggested. To the magnesic germanate obtained by Muller (33), referred to in the literature as ortogermanate, the following formula could be assigned.

$$[Mg(OH)]_2GeO_2(OH)_2 \equiv Mg_2GeO_4.2H_2O$$

which would correspond to a salt of the ion $GeO_2(OH)_2{}^{2-}$ with $MgOH^+$ which is formed at approximately pH 10.5, at which the reaction takes place, according to the equilibrium

$$Mg^{2+} + OH^- \rightleftharpoons MgOH^+$$

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[9] The calculation of the percentage for the different species is carried out as follows:

1. Calculating the values of Q_n for the different species begining with the values for K_n for the chosen value of I.
2. Calculating for each pH value

$$y = [H^+] = \text{ant log} (-pH - fH) \text{ (see note 4)}$$

3. Calculating $x = [Ge(OH)_4]$ by solving for each value of y (using C, total concentration of Ge, as a parameter) the equation

$$C = x\,(1 + Q_1/y + Q_2/y^2) + 8x^8\,Q_3/y^3$$

4. Solving the equation which is grade 8 by trial and errol with a precision of 0.001%.
5. After x is calculated, the following weight percents are obtained:

$$Ge(OH)_4 = 100x/C$$
$$GeO(OH)_3^- = 100xQ_1/y$$
$$GeO_2(OH)_2{}^{2-} = 100xQ_1/y^2$$
$$Ge_8O_{16}(H_2O)_5(OH)_3^{3-} = 800x^8Q_8,\ 3/y^3$$

6. The calculated values, at intervals of pH 0.1, are stored in an array.
7. A table is prepared, joining the corresponding points, which draws the graph % Ge(IV) against pH for the four species under consideration.

where the stability constant at ionic strength 3, see Smith and Martel (34), is 70.8. Therefore, at pH = 10.5, 2.2% of the magnesium is in the form of a hydroxilated complex.

By mixing in different proportions alkaline solutions of sodium germanate and aluminium chloride Schwarz and Trageser (35) had prepared a compound in which the ratio GeO_2/Al_2O_3 is practically 2, independently of the initial proportion of the mixture. Optimum precipitation conditions correspond to a pH= 7, assigning to the dry product at 100°C the emprical formula $Al_2O_3.2GeO_2.3H_2O$.

However, when adding Al $(OH)_3$ to germanic acid solutions, the Ge/Al ratio in the resulting product grows as the concentration of Ge in solution increases, up to an asymptotic value of 0.135, corresponding to the empirical formula $Al_2O_3.27GeO_2.nH_2O$.

In the case of the aluminium germanate, the formula for the salt which Schwarz and Trageser gave as $Al_2O_3.2GeO_2.3H_2O$, could also be written as $AlOHGeO_2(OH)_2$ corresponding to the germanate of the $AlOH^{2+}$ ion formed according to

$$Al^{3+} + OH^- \rightleftarrows AlOH_{2+}$$

with a stability constant of 2.04 · 10^8 at ionic strenght 1.

In spite of the enormous practical importance that the sorption of Ge by iron hydroxide has in the purification of electrolytic zinc, there are very few studies on this subject within the metallurgy of zinc.

Eudokimok and Kogan (36) studied the adsorption isotherms of diluted aqueous solutions of germanium dioxide by ferric hydroxide, and found that the molar ratio Fe/Ge always reached a value above 1 which, according to Tananaev and Chpipt (33), is related to the formation of a compound with the formula $[Fe(OH)_2]_2GeO_3$ and that the pH of the solution (which initially had a value of 6.9) changed up to a maximum value of 8.05.

Pakholkou et al. (38) studied the influence of the pH and the presence of various electrolytes in the sorption of GeO_2, on ferric hydroxide. This not very clear paper shows that the sorption capacity increases as the pH rises form 1 to 5, reaching a maximum between 4 and 6, and then decreasing rapidly. Comparing the sorption capacity of germanium with chloride, they indicated that the sorption of germanium occurs preferably as GeO_3H^- and, we quote, partially as $HGe_5O_{11}{}^{2-}$. From the analysis of infrared spectra of ferric hydroxide with sorbed germanate, he concludes that the reaction that takes place is

$$FeOOH + HGeO_3{-} <===> FeO^+HGeO_3{-} + OH^-$$

but this the reaction, could also be

$$2\ FeOOH + Ge(OH)_4 \rightleftarrows [Fe(OH)_2]_2GeO_2(OH)_2$$

This reaction could be preformed without any variation of the pH, contrary to the already mentioned data of Evdokimok and Kogan (36), according to whom, when iron hydroxide was added to the solution that had a pH of 6.9 this increased up to 8.5. We believe that this small evolution of the pH could be explained by the existence of ammonia adsorbed into the iron hydroxide and difficult to eliminate by washing. If this is so, the salt of the hydroxylate ion $Fe(OH)_2{+}$ reappears, formed as a consequence of the equilibrium

$$Fe(OH)_3 \rightleftarrows Fe(OH)_2{+} + OH^-$$

whose constant is 3.16 · 10^{-17}

The maximum sorption of Ge by the $Fe(OH)_3$ determined by Pakhoikov et al. (38) in approximately pH 5, coincides with the pH at which the predominant species among the different hydroxylate complexes of Fe(III) is $Fe(OH)_2^+$ (see Baes and Mesmer (2), page 237).

Complexes with hydroxilated compounds

Tchakirian (1) found that germanate dioxide in an aqueous solution reacts the manithol (and other polyhydroxilated alcohols) to form a strongly acid complex, a reaction which Cluley (37) used as a volumetric analytical method to evaluate Ge(IV) in solution. The method, which need not to be described here, has been used together with that of Muller for the quantitative analysis of Ge, because of its great simplicity and still appears in recent publications. The reaction that takes place is:

$$2L(OH)_2 + Ge(OH)_4 \rightleftarrows (LO_2)_2GeOH^- + 3\ H_2O + + H^+$$

In the case of manithol, the equilibrium quotient Q at an ionic strength of 0.1 is 8.91 · 10^{-5}, rising to 1.12 · 10^{-4} when the ionic strength rises to 0.5 [see Antikainen (40) and Petterson (41), although the highest value tabulated corresponds to ribose, 3.47 · · 10^{-3} according to Antikainen and Huttunen (42).

The reactivity of germanic acid with compounds containing in hydroxile groups is not limited to polyalcohols. Complexes formed with polyphenols are even more stable:

$$3\ PhH_2 + Ge(OH)_4 \rightleftarrows GePh_3{}^{2-} + 4\ H_2O + 2\ H^+$$

where log Q is (at ionic strength 0.1) −1.2 for pyrocatecol and −0.6 for pyrogalol, Stejskal and Bartusek (43), although for benzene derivatives, for example for chloro-1,2-dihydroxibenzene, Meilleur and Benoit (44), values as high as 6.67 may be reached.

Precipitation with tannine, used both as an analytical and an industrial method, is based on a reaction of this type since, as it is known, tannine (galotannin) contains a digaloilated glucose as its active principle.

Dicarboxylic acids also form very stable complexes with germanic acid. Thus the oxalic acid forms the complex $Ge(C_2O_4)_3{}^{2-}$ which is extraordinarily soluble (in the literature the possibility is mentioned of obtaining syrup solutions with 180 gr/l of GeO_2 (45)).

Finally, we should mention the hydroxicarboxylic acids such as tartaric, lactic, mandelic and malic which in anionic form give very stable complexes with germanic acid, especially the former. Thus, according to Vartapetian (46).

$$Ge(OH)_4 + C_4H_5O_6{-} \rightleftarrows GeOC_4H_3O^- + 3\ H_2O$$

where (for an ionic strenght 1) Q = 1.75 · 10^{-5}.

DISCUSSION

Up to now, we have mentioned as objectively as possible the most important works that we have found referring to the subject under discussion. To avoid interferring with the exposition and to ensure objectivity, at certain points a reference was made in the notes, where we give our own opinion on certain statements, or where treat particular points in greater detail.

Before entering into the discussion of the subject, we think it appropriate to recapitulate, perhaps more subjectively, on what has gone before, in order to have an overall picture of the problem.

Recapitulation of results

The data offered may, in our opinion, be summarised succinctly by the following points:

1. Germanium dioxide increases its solubility through the addition of sodium or potasium hydroxide in the proportion of approximately 5 at-g of Ge for every 2 mol of hydroxide, although this 5/2 ratio might, because of experimental errors, be 7/3 and even 8/3. But, and this is only pointed out by Pugh since the other researchers do not take it into account, the solutions show a marked Tyndall effect.

2. However, in presence of manitol (and other polyhydroxilate alcohols) the solubility of GeO_2 is 1/2 mol per mol of NaOH.

3. The mathematical analysis of the neutralization curves of the germanic acid at different concentrations, and the corresponding calculation of errors, leads to the existence of a species in solution with 8 atoms of germanium and three negative charges.

4. There is an insoluble species formed nearly the same pH at which the maximum stability of the possible polygermanate ion occurs; however, the Ge/M ratio in the salt is 7/3 instead of 8/3. When this salt is treated at high temperatures with its mother liquid (pH ≈ 9), it evolves into another species in which the ratio is 9/4. On the other hand any salt with a ratio of 8/3 has been identified.

5. Finally, it is observed that while for monovalent cations (alkalines, Ag and Tl^+) a germanate has been identified in the proportion Ge/M= 7/3 but not 8/3, for some di- and trivalent ones (Mg, Al, Fe) the Ge/M proportion is lower and corresponds to more simple numbers: 1/2 for Mg and Fe and 1 for Al.

The analysis of the cases presented indicates that in all of them the anion of the salt may be the germanate ion, $GeO_2(OH)_2{}^{2-}$ even though precipitation occurs at a lower pH than that for alkaline polygermanate (pH 7 for aluminium against 9 for potasium). Another datum to take into account is that in the three cases presented the cation appears as a complex hydroxylate.

Mechanism of the disolution of germanate dioxide in alkalies

The experimental results shown in figure 1 unquestionably indicate that the germanium oxide dissolves in sodium hydroxide (or other alkaline hydroxide) in the proportion of 5 mol of germanium oxide per 2 mol of hydroxide (or at values very close to these). Given the importance of the datum, we have repeated the experiment, measuring the pH with a glass electrode and also analysing the sodium content in the solution. We saw that, on adding 50 mmol/l of NaOH to a pulp formed by an excess of GeO_2 in distilled water, the pH rose to a value of around 10.5 then decreased rapidly, stabilising at the end of 2 minutes at a value of 7.3; the solution became cloudy and remained so for 1 week, being impossible to eliminate this cloudiness by filtering. The analysis cf the Ge in solution gave 12.5 gr/l and the sodium 1.12 gr/l, figures which, within experimental error, correspond to what might be expected form the data in figure 1. However, the pH did not coincide with that what could be expected, 7.6, under the hypothesis of polygermanate.

Since there unquestionably exists a species in solution that has at least 5 atoms of germanium and 2 negative charges, and since whenever hydroxylated species are in solution this opecies disappears [it is only necessary to add manitol, as Tschakirian (1), observed, for the Ge/Na ratio to fall to 1], and since the di- and trivalent cations are capable of forming $M(OH)_n{}^m$ complexes, giving a Ge/M ratio of 1 or 1/2, it is not hazardous to suposse that the germanic acid itself complexes with germanate ion according to a reaction that we could write as

$$GeO_2(OH)_2{}^{2-} + 4Ge(OH)_4 \rightleftharpoons GeO_2(OH)_2[Ge(OH)_4]_4{}^{2-} \quad [6]$$

This complex which contains 5 atoms of germanium and 2 negative charges and, leaving out the water molecules, could be written as

$$Ge_5O_{11}.9H_2O^{2-}$$

cannot be a polymer, whose kinetic of formation would be quite diferent. The species, considered as a complex, does not oblige us to state necessarily that the 5 or 8 germanic acids are found simultaneously at a point in space and that they immediately lose the 3 protons. It is now only necessary that the germanate already formed, continuously increase its $Ge(OH)_4$ bindings until reaching the coordination index of 4 which, in turn, could be in accordance with the data of Antikainen (31) who identified two species, Ge_2- and Ge_3-, which could well be $Ge_4{}^{2-}$ and $Ge_4{}^{2-}$.

At first the hypothesis appears rather surprising, but knowing the affinity of germanium for molecules with hydroxyl groups we do not think impossible that the germanic acid should act in the way which we have shown above that the oxalic acid acts, for example.

This, as we shall see, can be explained by all the experimental work that we have presented:

— Naturally, the disolution of the germanium dioxide in sodium hydroxyde in the proportion 5/2 is explained.

— There is an explanation for the precipitation of the germanates such as that of the aluminium through a greater affinity of the germanate ion for $AlOH^+$ than for the germanic acid which remains free, and in the alkaline medium in which it is present would give new germanate, until the

— The precipitation of the Nowotny and Wittmann salt, $M_3HGe_7O_{16}.4H_2O$ is explained, following Carpeny et al. (30), allowing that two consecutive reactions take place: the formation of $K_2Ge_5O_{11}$ and the alkaline transformation

$$7\,K_2Ge_5O_{11} + KOH \rightarrow 5\,K_3HGe_7O_{18}$$

The fact that a pentagermanate is formed with the monovalent metals, and not a germanate as occurs with the di- and trivalents is easily explained by returning to the affinity of germanate for hydroxyl groups. In fact, in the case of cations ofa valence 2 or more, it is always possible to obtain a cation with formula MOH^+ for the divalents, and MOH^{2+} for trivalents, while in the case of the monovalents either the neutral species MOH would be obtained, or an anion $M(OH)_2^-$, incapable of forming salts with the germanate anion. Therefore the precipitation of the germanates of the monovalent cations can only take place as a combination of the pentagermanate ion and the monovalent cation.

Finally, the existence of the pentagermanate ion within a narrow margin of pH is a direct consequence of the need for coexistence between the germanic acid and the germanate ion. At a low pH, only germanic acid exists, while at a higher pH there are only germanate ions.

Calculation of the stability constant

Without going into a detailed experimental study here, it is possible to see how, based on the hypothesis of the formation of the complex, it is possible to calculate its stability constant, and that this is the same as can be deduced from potenciometric measurements.

In the presence of $GeO_2(s)$, the equilibrium is given

$$GeO_2(s) + 2\,H_2O \rightleftharpoons Ge(OH)_4$$

and in accordance with the solubility measurements

$$[Ge(OH)_4] = 0.0437$$

On adding sodium hydroxid to the soltuion, the reaction which take place is

$$Ge(OH)_4 + 2\,OH^- \rightleftharpoons GeO_2(OH)_2{}^{2-}$$

and, according to its equilibrium constant, K_2

$$[GeO_2(OH)_2{}^{2-}] = 5.51\cdot10^{-20}/[H^+]^2$$

On the other hand, from [6]

$$[Ge_5O_{11}{}^{2-}] = K_4[Ge(OH)_4]^4[GeO_2(OH)_2{}^{2-}]$$

If we presume a strong displacement of the equilibrium to the right, i.e., if $K_4 >> 1$, then the concentration of pentagermanate will be that of Ge (IV) than less 0.0437.

In accordance with the measurement previously indicated, the following values are given

$$[Ge(IV)] = 12.5\ g/l = 0.1724\ M$$

and therefore

$$[Ge_5O_{11}{}^{2-}] = 0.1724 - 0.0437 = 0.129\ M$$

$$pH = 7.33 \quad \rightarrow \quad [H^+] = 4.68.10^{-8}\ M$$

form which

$$K_4 = 1.4.10^{13} \quad (\log K_4 = 13.1)$$

The value of K_4 may be related to that of K_5 of Lorijsen-Tyssedre of the reaction [1] that we write in actual terminology

$$K_5 = \frac{[Ge(OH)_4]^3[GeO(OH)_3{}^-]^2}{[Ge_5O_{11}{}^{2-}]} \qquad [7]$$

and from [6]

$$K_4 = \frac{[Ge_5O_{11}{}^{2-}]}{[Ge(OH)_4]^4[GeO_2(OH)_2{}^{2-}]} \qquad [8]$$

where

$$K_4 = \frac{K_1{}^2}{K_5 - K_2} \quad \text{or} \quad \log K_4 = -\log(K_5/K_1{}^2) - \log K_2$$

According with the experimental value of Lorijsen-Teyssedre (20)

$\log(K_5/K_1{}^2) = 9.5 \pm 0.4$[10]

and, as $\log K_2 = -21.9 \pm 0.1$,

$$\log K_4 = 12.4 \pm 0.5$$

a figure which coincides with the order magnitude and whose difference may be explained taking into account that K_5 suffers from certain numerical errors (see notes 4 and 5) and that it is calculated for ionic strenght 0.3.

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[10] The accuracy of K_4 was estimated by us from the figure of the paper under reference (20).

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