5. V.I. Safonova, G.P. Kuznetsova, and B.D. Stepin, Zhur. Neorg. Khim., 10, 2351 (1965) [Russ. J. Inorg. Chem., No. 10 (1965)].

6. L.L. Makarov and A.G. Pankov, Zhur. Fiz. Khim., 36, 2241 (1962) [Russ. J. Phys. Chem., No. 10 (1962)].

Lomonosov Moscow Institute   Received 12th June 1970
of Fine Chemical Technology
All Union Scientific Research
Institute for Chemical Reagents
and Highly Pure Materials

State of Germanium(IV) in Acid Solutions

I.I. Alekseeva and I.I. Nemzer

The state of germanium(IV) in acid solutions at concentrations above 10^{-4} M has been studied potentiometrically. Polynuclear germanium(IV) complexes of the $Ge[Ge(OH)_n]_l^{(4+3n)+}$ type are found to predominate at pH 0–2, where n can vary from 1 to 10. In the pH 2–6 region the solution contains only mononuclear complexes of the $Ge(OH)_i^{(4-i)+}$ type, or a single mononuclear species.

Our knowledge of the state of germanium in acid solutions is inadequate[1]. Nazarenko and coworkers[2-5], who published the only detailed study of the state of germanium(IV) in dilute acid solutions, showed that various hydroxo complexes of composition $Ge(OH)_i^{(4-i)+}$ are present in solutions of pH 1–7, and that the Ge^{4+} ion appears when the acidity is high enough[5]. The work was done at germanium(IV) concentrations $\leqslant 10^{-4}$ M, i.e. in solutions where polymerisation is precluded and polynuclear complexes cannot exist. There is no information on the state of germanium(IV) in more concentrated solutions. Our aim was to study the state of germanium(IV) in acid solutions at higher concentrations, i.e. under conditions leading to the formation of polynuclear as well as mononuclear germanium(IV) complexes.

Stepwise complex formation in the presence of polynuclear complexes, and hydrolytic reactions of the type

$$qMe^{m+} + pH_2O \rightleftarrows Me_q(OH)_p^{(qm-p)+} + pH^+$$
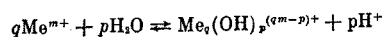
were studied by a potentiometric method based on Sillén's hypothesis[6].

EXPERIMENTAL

Four series of potentiometric titrations were carried out (sodium germanate solutions against acid solutions of germanium(IV)). The reversibility of the process was tested by titrating in both directions. The potentiometer was of the LPU-01 type, with a glass indicator electrode and a saturated calomel reference electrode.

The sodium germanate solutions had pH 10–11, the acid solutions of germanium(IV) had pH 0–1. The concentration of germanium(IV) was held constant in each series of experiments: 5.0×10^{-3} M in series I, 1.0×10^{-2} M in series II, 2.0×10^{-2} M in series III, and 3.0×10^{-2} M in series IV.

The measurements were made in solutions of high and constant ionic strength (1 M sodium perchlorate). The required total concentration of hydrogen ions (c_{H^+}) was obtained by adding perchloric acid, and calculated analytically. The equilibrium concentration of free hydrogen ions ($[H^+]$) was measured potentiometrically.
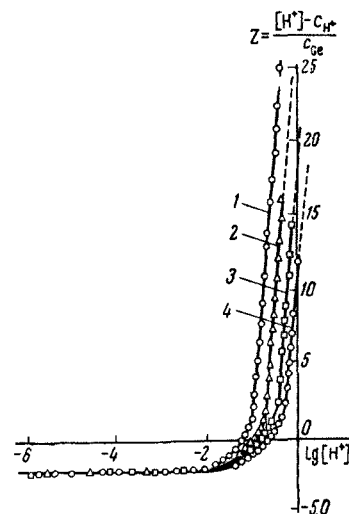

Figure 1. Plots of Z against $\lg[H^+]$. c_{Ge}: 1) 5.0×10^{-3}, 2) 1.0×10^{-2}, 3) 2.0×10^{-2}, 4) 3.0×10^{-2} mole litre^{-1}.
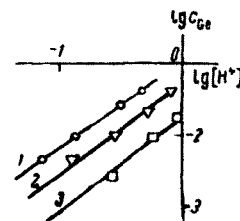

Figure 2. Plots of $\lg c_{Ge}$ against $\lg[H^+]$. 1) $Z = 1$, $\tan \alpha = 1.0$; 2) $Z = 5$, $\tan \alpha = 1.1$; 3) $Z = 10$, $\tan \alpha = 1.0$.

DISCUSSION

The first requirement was to identify the types of complex involved in the present system. The average number of protons (Z) contributed by each germanium(IV) ion was calculated from the experimental quantities c_{Ge}, c_{H^+}, and $[H^+]$:

$$Z = \frac{[H^+] - c_{H^+}}{c_{Ge}} .$$

Plots of Z against $\lg[H^+]$ were constructed (Fig. 1) for different values of c_{Ge}, with the calculated values of Z (Table 1). Evidently, Z is a function of c_{Ge} as well as of $\lg[H^+]$. Hence, we may conclude that polynuclear

Table 1. Experimental and calculated values needed to apply Sillén's graphical method.

$c_{Ge} = 5.0 \cdot 10^{-3}$ M				$c_{Ge} = 1.0 \cdot 10^{-2}$ M				$c_{Ge} = 2.0 \cdot 10^{-2}$ M				$c_{Ge} = 3.0 \cdot 10^{-2}$ M			
c_{H^+}	pH	[H+]	Z	c_{H^+}	pH	[H+]	Z	c_{H^+}	pH	[H+]	Z	c_{H^+}	pH	[H+]	Z
0.1820	0.62	0.2400	11.60	0.4170	0.28	0.5320	11.50	0.4550	0,25	0.5620	5.35	0.4540	0.24	0.5750	6.37
0.1665	0.67	0.2140	9.40	0.3850	0.32	0.4800	9.50	0.4170	0,29	0.5130	4.80	0.4160	0.28	0.5250	3.60
0.1330	0.75	0.1780	9.08	0.3340	0,38	0.4170	8.30	0.3570	0,36	0.4370	3.85	0.3570	0.36	0.4370	2.67
0.1250	0.78	0.1660	8.20	0.2630	0,48	0.3320	6.90	0.3340	0.40	0.3980	3.20	0.3350	0.40	0.3980	2.16
0.1110	0.84	0.1450	6.80	0.2380	0,53	0.2950	5.70	0.2630	0.50	0.3160	2.65	0.3130	0.45	0.3550	1.43
0.1050	0.87	0.1350	5.80	0.2170	0,58	0.2660	4.90	0.2500	0.53	0,2950	2.25	0.2940	0.49	0.3240	1.00
0.0910	0.94	0.1140	4.60	0.2000	0,62	0.2400	4.00	0.2380	0.56	0.2760	1.90	0.2780	0.52	0.3020	0.80
0.0800	1.00	0.1000	4.00	0.1820	0,68	0.2120	3.00	0.2270	0.59	0.2570	1.50	0.2500	0.58	0.2630	0.43
0.0667	1.10	0.0790	2.54	0.1540	0,76	0.1740	2.00	0.2080	0.63	0.2350	1.35	0.2380	0.63	0.2350	—0.10
0.0572	1.18	0.0660	1.76	0.1180	0,88	0.1330	1.55	0.2000	0.67	0,2140	0.70	0.2080	0.71	0.1950	—0.43
0.0500	1.27	0.540	0.74	0.0885	1.00	0.1000	1.10	0.1820	0.72	0.1900	0.40	0.1820	0.79	0.1620	—0.67
0.0400	1.40	0.0390	—0.04	0.0715	1.14	0.0725	0.10	0.1660	0.78	0.1640	—0.15	0.1430	0.97	0.1080	—1.20
0.0308	1.59	0.0357	—1.00	0.0500	1.40	0.0398	—1.02	0.1430	0.86	0.1380	—0.25	0.1110	1.24	0.0570	—1.78
0.0236	1.80	0.0160	—1.54	0.0400	1.61	0.0245	—1.55	0.1180	0.97	0.1070	—0.55	0.0926	1.54	0.0290	—2.12
0.0187	2.00	0.0100	—1.74	0.0364	1.73	0.0186	—1.78	0.1000	1.10	0.0790	—1.02	0.0715	2.31	0.0050	—2.22
0.0142	2.50	0.0030	—2.22	0.0267	2.2	0.0063	—2.04	0.0885	1.27	0.0540	—1.75	0.0703	2.53	0.0030	—2.24
0.0127	3.43	0.0004	—2.48	0.0236	3.06	0.0009	—2.27	0.0465	3.00	0.0003	—2.32	0.0690	3.17	0.0007	—2.28
0.0125	4.75	—	—2.50	0.0220	5.15	—	—2.20	0.0460	4.00	—	—2.30	0.0685	5.00	—	—2.28
0.0119	6.00	—	—2.40	0.0222	6.15	—	—2.22	0.0554	6.90	—	—2.27	0.0677	6.00	—	—2.26
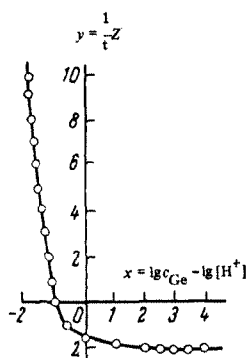
Figure 3. Plot of y against x. $y = \frac{1}{t}Z$; $x = \lg c_{Ge} - \lg[H^+]$.

Figure 4. Plot of pH + $\lg[Ge^{4+}]$ against $\lg[Ge_{n+1}(OH)_n]^{3n+}$.

complexes are formed in these solutions*. Mononuclear complexes are significant only at very low Z values and in the pH range 2–6.
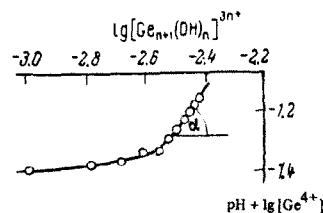
The curves in Fig. 1 for different concentrations of germanium(IV) are practically parallel, thus enabling the quantity R (defined as $\Delta \lg c_{Ge}/\Delta \lg[H^+] = $ const) to be calculated[6] from the parallel shift of the lines. This is done in Fig. 2, by plotting $\lg c_{Ge}$ against $\lg[H^+]$ at three values of Z (1, 5, and 10): the slope of the three straight lines, which gives[6] the value of $-R$, is found to be 1.0, 1.1, and 1.0 respectively. Allowing for the experimental and computational errors, we may conclude that $-R = 1.0$.

The hydrolysis reaction is described by the equation

$$q\,Ge^{4+} + pH_2O \rightleftarrows Ge_q(OH)_p^{(4q-p)+} + pH^+$$

This hydrolysis is of the cationic type, since the acidity of the solution increases with the concentration of germanium(IV) (see Table 1). Hence, the resulting germanium(IV) complexes can be assumed to be of the form $Ge[Ge(OH)_t]_n^{[4+(4-t)n]+}$, where $t = -R = $ const.[6] In the
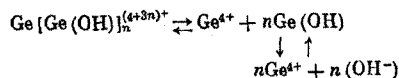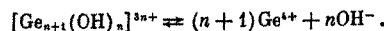
present system $t = 1.0$; n (the number of branches in the complex) can have any value for which q and p are integers. The quantity Z can be expressed as a function of x, where $x = \lg c_{Ge} - t\lg[H^+]$.[6] If t has been evaluated correctly, all the points in the plot of y against x (where $y = \frac{1}{t}Z$) should lie on the same curve. Our experimental plot of y against x is shown in Fig. 3: it is clear that all the points lie smoothly on the same curve. Thus, the plot in Fig. 3 is evidence that germanium(IV) complexes of the type $Ge[Ge(OH)]_n^{(4+3n)+}$ are present in solution.

The value of n was found as follows. The dissociation of the above germanium complex can be expressed as

$$Ge[Ge(OH)]_n^{(4+3n)+} \rightleftarrows Ge^{4+} + nGe(OH)$$
$$\downarrow \uparrow$$
$$nGe^{4+} + n(OH^-)$$

or

$$[Ge_{n+1}(OH)_n]^{3n+} \rightleftarrows (n+1)Ge^{4+} + nOH^-.$$

The dissociation constant of this complex is

$$K_{diss} = \frac{[Ge^{4+}]^{n+1}[OH^-]^n}{[Ge_{n+1}(OH)_n]^{3n+}} \quad . \tag{1}$$

Taking logarithms, and assuming that $lg \dfrac{K_{diss}}{n} \simeq const = A$, we arrive at the expression

$$pH + lg[Ge^{4+}] = A' + \frac{1}{n} lg[Ge_{n+1}(OH)_n]^{3n+} \qquad (2)$$

where $A' = A + 14$. Taking $lg[Ge_{n+1}(OH)_n]^{3n+}$ as the independent variable, and $pH + lg[Ge^{4+}]$ as the dependent variable, Eqn. (2) describes a curve such that the slope at every point is equal to $1/n$. The graph was constructed (Fig. 4) from data calculated from the experimental results (Table 2). The slope of the curve varies smoothly from 0.1 to 2.0, showing that n varies from 1 to 10.

Table 2.

$[Ge_{n+1}(OH)_n]^{3n+} \cdot 10^3$	$lg[Ge_{n+1}(OH)_n]^{3n+}$	$[Ge^{4+}] \cdot 10^3$	$lg[Ge^{4+}]$	pH	$pH + lg[Ge^{4+}]$
1.00	−3.000	4.00	−2.398	1.00	−1.398
1.67	−2.780	3.33	−2.477	1.10	−1.377
2.14	−2.670	2.86	−2.543	1.18	−1.363
2.50	−2.602	2.50	−2.602	1.27	−1.333
2.78	−2.555	2.22	−2.654	1.33	−1.324
3.00	−2.511	2.00	−2.700	1.40	−1.300
3.18	−2.497	1.82	−2.740	1.47	−1.270
3.33	−2.478	1.67	−2.778	1.54	−1.238
3.46	−2.460	1.54	−2.812	1.59	−1.220
3.57	−2.447	1.43	−2.845	1.64	−1.205
3.67	−2.435	1.33	−2.876	1.70	−1.176
3.75	−2.424	1.25	−2.903	1.75	−1.153
3.82	−2.418	1.18	−2.928	1.80	−1.128

Our overall conclusion is that germanium(IV) ions at concentrations above 10^{-4} M and pH 0–2 are hydrolysed with formation of polynuclear complexes of the $Ge[Ge(OH)]_n^{(4+3n)+}$ type, where n varies from 1 to 10. In the region of pH 2–6, the experimental results (Fig. 1) suggest the presence of either a number of mononuclear hydroxo complexes of the $Ge(OH)_i^{(4-i)+}$ type, or a single homonuclear species such as pentagermanic acid[5].

REFERENCES

1. I. V. Tananaev and M. Ya. Shpirt, "Khimiya Germaniya" (The Chemistry of Germanium), Izd. Khimiya, Moscow, 1967.
2. V. A. Nazarenko, Symposium "Metody Opredeleniya i Analiza Redkikh Elementov" (Methods of Determination and Analysis of the Less-common Elements), Izd. Akad. Nauk SSSR, Moscow, 1961.
3. V. A. Nazarenko and A. M. Andrianov, Uspekhi Khim., 34, 1313 (1965) [Russ. Chem. Rev., No. 8 (1965)].
4. A. M. Andrianov and V. A. Nazarenko, Zhur. Neorg. Khim., 11, 1527 (1966) [Russ. J. Inorg. Chem., No. 7 (1966)].
5. V. A. Nazarenko and G. V. Flyantikova, Zhur. Neorg. Khim., 13, 1855 (1968) [Russ. J. Inorg. Chem., No. 7 (1968)].
6. G. L. Shlefer, "Kompleksoobrazovanie v Rastvorakh" (Complex Formation in Solutions), Izd. Khimiya, Moscow–Leningrad, 1964.
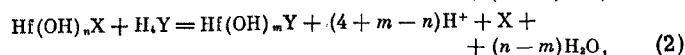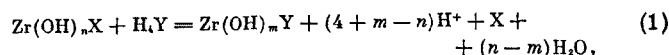
Kinetics and Mechanism of the Replacement of Xylenol Orange by Ethylenediaminetetra-acetate in Complexes of Zirconium and Hafnium with Xylenol Orange

L.I.Budarin, R.B.Suchkova, and K.B.Yatsimirskii

The kinetics and mechanism of the replacement of Xylenol Orange by ethylenediaminetetra-acetate in complexes of zirconium and hafnium with Xylenol Orange have been studied by the stopped-flow method. It has been shown that these reactions are of second order with respect to the concentrations of the complex of zirconium (hafnium) with Xylenol Orange and ethylenediamine-tetra-acetate. It is suggested that the reaction takes place by an associative mechanism. The rate-determining stage is the formation of the complex with mixed ligands $MX + EDTA \xrightarrow{k_1} MX(EDTA)$, where X = Xylenol Orange and EDTA = ethylenediaminetetra-acetate. The conditional rate constants $k_{cond} = k_1[EDTA]$ have been calculated. It has been established that the mechanisms of the reactions of the zirconium and hafnium complexes are the same.

The kinetics of the reactions of zirconium and hafnium complexes have been insufficiently studied, apparently because the reaction rates are influenced markedly by the state of the ions of these elements in solution[1,2]. Under conditions in which polynuclear hydrolysed zirconium (hafnium) ions exist in solution, the kinetics studied[2,3] are in fact the kinetics of the fairly slow decomposition of the polynuclear ions into simple ions in the reaction with powerful complex-forming reagents. The difficulty of these studies lies in the identification of the polynuclear ions taking part in the reactions. On the other hand, mononuclear zirconium (hafnium) ions are characterised by rapid complex formation[2], and the study of their rates requires special methods.

The present paper deals with the kinetics and mechanism of the replacement of Xylenol Orange (X) by ethylene-diaminetetra-acetate (EDTA) in complexes of zirconium (hafnium) with Xylenol Orange:

$$Zr(OH)_nX + H_4Y = Zr(OH)_mY + (4 + m - n)H^+ + X + \qquad (1)$$
$$+ (n - m)H_2O,$$

$$Hf(OH)_nX + H_4Y = Hf(OH)_mY + (4 + m - n)H^+ + X + \qquad (2)$$
$$+ (n - m)H_2O,$$

where X represents Xylenol Orange (3,3'-bis-di(carboxy-methyl)aminomethyl-o-cresolsulphophthalein), protonated to different extents, and H_4Y the undissociated form of EDTA. We first verified that under the conditions described below, equilibria (1) and (2) are displaced almost completely towards the formation of the complexes of zirconium and hafnium with EDTA.

EXPERIMENTAL

Reactions (1) and (2) were studied by the stopped-flow method, with spectrophotometric recording[4]. A glass light filter with $\lambda_{eff} = 540$ nm was used. The reagents used were "pure" grade zirconium oxide chloride and hafnium oxide chloride, both recrystallised from 8 M