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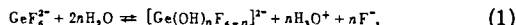
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HYDROLYSIS OF POTASSIUM HEXAFLUORO-GERMANATE IN AQUEOUS SOLUTION

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Schmitt *et al.*¹ measured the electrical conductivity and pH of aqueous solutions of several hexafluoro-complexes, including the hexafluorogermanates of potassium, rubidium, and caesium at 25°. The results confirm qualitatively the extensive hydrolysis of GeF_6^{2-} in dilute solutions. Because of the marked autocatalytic character of the hydrolysis of GeF_6^{2-} ,² it may be assumed that in spite of the slowness of the initial stages of the process, the results of the American authors were close to the equilibrium values. Their calculated degrees of hydrolysis of GeF_6^{2-} are unreliable, however. They assumed that hydrolysis took place in one stage



and that the concentrations of F^- and H_3O^+ were identical. They calculated $[\text{H}^+] = [\text{F}^-]$ from the pH of the solution and then calculated the HF concentration from the dissociation constant of HF. The degree of hydrolysis was obtained by dividing the sum $[\text{F}^-] + [\text{HF}]$ by the total hexafluorogermanate concentration. This method leads to erroneous results when the concentrations $[\text{H}^+]$ and $[\text{F}^-]$ are not equal, which may occur if hydroxofluoroquogermanates are formed; moreover, it is shown below that the materials used by Schmitt *et al.*¹ apparently contained traces of fluoride. We established² that the rate of hydrolysis of GeF_6^{2-} at low temperatures is low and independent of the OH^- concentration, whereas other fluorogermanates are rapidly neutralised by alkali. This allows an analytical determination of GeF_6^{2-} in the presence of its hydrolysis products, and the method has been used successfully in earlier work^{2,3}.

The present paper describes the determination of the concentration dependence of the equilibrium degree of hydrolysis of K_2GeF_6 solutions at 0° and 25°.

EXPERIMENTAL

A purified recrystallised³ specimen of K_2GeF_6 and carbonate-free NaOH solution³ were used. The original 0.01121 *m* K_2GeF_6 solution (*m* denotes molality) was in twice-distilled water; more dilute solutions were obtained by adding the required weight of twice-distilled water, and were stored in polyethylene containers at room temperature. Before measuring the degree of hydrolysis and pH, we kept the solutions for a long time in polyethylene vessels in a thermostat (15–20 h at 0° or 2–3 h at 25°).

Thanks to the marked catalytic action of H^+ on the rate of decomposition and formation of GeF_6^{2-} , the above periods ensured that equilibrium was attained. This was confirmed by analysing a series of specimens taken after longer time intervals. Since the degree of hydrolysis of GeF_6^{2-} decreases as the temperature is reduced, we approached the equilibrium state at 0° from the direction of GeF_6^{2-} formation. Similar values for the equilibrium degree of hydrolysis were obtained when equilibrium was approached from the direction of GeF_6^{2-} hydrolysis.

Specimens of the solutions were removed in pipettes coated with a melt of polyethylene and paraffin wax and brought to the temperature of the solution, and calibrated from the weights of the solutions studied. The equilibrium degree of hydrolysis of GeF_6^{2-} at 0° was found by a direct titration of the hydrolysis products². At 25°, because of the greater mobility of the equilibrium, the equilibrium state was "frozen" and the system was analysed as described earlier³.

In parallel with the titrimetric determination of the hydrolysis of GeF_6^{2-} in solution, the pH was measured with a quinhydrone electrode, saturated calomel reference electrode, and saturated KCl salt bridge. The measuring cell was constructed so that it could be completely immersed in the thermostat liquid and that the K_2GeF_6 solution came into contact with polyethylene only. The e.m.f. was measured with a PPTV-1 potentiometer and GZP-47 mirror galvanometer as null-instrument. To measure the pH of the equilibrium systems at 0°, the cell was kept in a Dewar flask with melting ice, and at 25°, in a TS-15 thermostat. The calomel electrode was kept at these temperatures for 2 d before the start of the measurements. Error in the pH determinations was due chiefly to diffusion potentials, and estimation of the latter by means of Henderson's formula showed that the observed pH values (Tables 1 and 2) are reliable up to ~0.02.

TABLE 1. Equilibrium degree of hydrolysis and pH of aqueous potassium hexafluorogermanate solutions at 0°.

Specimen No.	K_2GeF_6 molality, 10^{-6}	Degree of hydrolysis α , determined by method		pH	$1-\alpha^{2*}$	$10^6 K_2^{***}$	Specimen No.	K_2GeF_6 molality, 10^{-6}	Degree of hydrolysis α , determined by method		pH	$1-\alpha^{2*}$	$10^6 K_2^{***}$
		A*	3**						A*	3**			
1	11.21	0.215	0.215	3.06	0.932	1.48	17	1.50	0.606	0.603	3.05	0.798	1.01
2	11.21	0.217	0.216	—	0.934	1.52	18	1.28	0.650	0.649	—	0.788	1.02
3	10.00	—	—	3.03	—	—	19	1.225	—	—	3.03	—	—
4	8.91	—	—	3.01	—	—	20	0.98	0.726	0.740	3.03	0.750	1.04
5	8.50	0.258	0.256	—	0.923	1.52	21	0.91	0.754	0.757	3.06	0.740	1.09
6	7.60	0.274	0.275	2.99	0.919	1.50	22	0.85	0.772	0.779	3.01	0.730	1.10
7	7.12	0.289	0.289	—	0.918	1.53	23	0.81	0.784	0.790	3.14	0.730	1.09
8	7.00	—	—	3.01	—	—	24	0.70	0.849	0.844	3.18	0.719	1.40
9	5.55	0.313	0.317	3.03	0.898	1.26	25	0.70	0.836	0.839	3.21	0.708	1.25
10	4.9	—	—	3.02	—	—	26	0.62	0.868	0.869	3.16	0.692	1.32
11	4.38	—	—	2.99	—	—	27	0.49	0.914	0.922	—	0.652	1.39
12	3.63	0.389	0.390	2.97	0.870	1.12	28	0.46	0.948	0.951	3.23	0.640	2.33
13	2.49	0.466	0.466	3.01	0.840	0.99	29	0.43	0.962	0.956	3.29	0.616	2.45
14	2.45	—	—	3.03	—	—	30	0.28	0.963	0.988	3.23	0.510	1.79
15	2.31	0.477	0.485	3.03	0.832	0.95	31	0.21	1.00	0.980	3.36	0.422	1.81
16	1.92	0.523	0.522	3.01	0.815	0.88							

* Degree of hydrolysis determined by titrating the hydrolysis products in the specimen with alkali at 0°.

** Degree of hydrolysis determined from the quantity of alkali used in the titration when the undecomposed GeF_6^{2-} remaining in the specimen was boiled.

*** See p. 754.

TABLE 2. Equilibrium degree of hydrolysis and pH of aqueous potassium hexafluorogermanate solutions at 25°.

Specimen No.	K ₂ GeF ₆ molality, 10 ³ c ₀	Degree of hydrolysis z, determined by method		pH	1-γ ^{***}	10 ⁴ K ₁ ^{***}
		B*	C**			
1	10.0	0.334	0.333	3.07	0.978	5.5
2	7.0	0.394	0.389	3.08	0.970	4.7
3	4.9	0.492	0.486	3.12	0.964	5.3
4	2.45	0.736	0.734	3.17	0.947	8.5
5	1.225	0.985	—	3.37	~0.911	(87.1)

* Analogous to method B in Table 1.

** Degree of hydrolysis determined from the ratio of the volume of alkali used in the titration when the undecomposed GeF₆²⁻ remaining in the specimen was boiled to the total volume of alkali used in the titration of the specimen with boiling.

*** See p. 754.

RESULTS

The results are in Tables 1 and 2 and Fig. 1. The small squares in Fig. 1 denote the points obtained as the limiting values of the degree of hydrolysis of K₂GeF₆ solutions in the study of the kinetics of this process. That they lie on the main curve confirms that the equilibrium state was reached.

Fig. 1 also gives for comparison the degree of hydrolysis calculated by the American authors¹. These differ considerably from the true values, because of the erroneous assumptions made in the calculations and also because the salt specimens used were apparently contaminated with fluorides. This follows from the methods of preparation used, and is confirmed by the fact that the measured pH values are higher than the true ones and decrease with dilution, although the general laws of chemical equilibrium should have led us to expect an increase in pH, as we in fact observed in the most dilute solutions at 0° and throughout the whole concentration range at 25°.

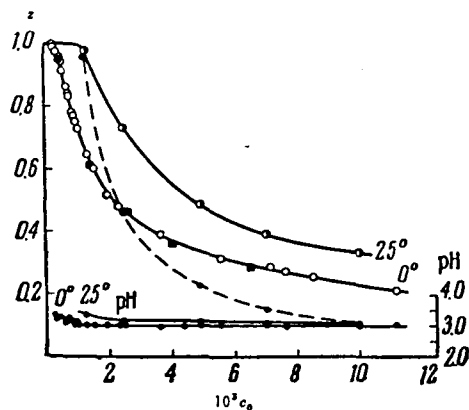
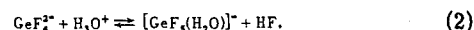


Fig. 1. Dependence of the equilibrium degree of hydrolysis and pH on the molal concentration of K₂GeF₆ solutions at 0° and 25°. The broken line gives the degree of hydrolysis at 25° according to the results of Schmitt *et al.*¹

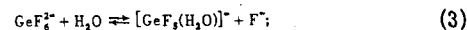
The increase in the degree of hydrolysis, calculated by the American workers, with fall in concentration is exaggerated by the effect of the observed decrease in pH.

A curious feature is that the equilibrium values of the degree of hydrolysis of GeF₆²⁻ at both 0° and 25° are much higher than those for SiF₆²⁻ at 11°,⁴ although the thermal stability of the salts⁵ and the kinetics of decomposition of SiF₆²⁻⁶ and GeF₆²⁻² indicate that GeF₄ is a stronger acceptor of F⁻ ions than SiF₄. This is probably due to the fact that the fluoroaquo-germanates [GeF₅(H₂O)]⁻ or [GeF₄(H₂O)₂]⁻ formed by the removal of F⁻ are stronger protonic acids than the analogous silicon compounds; the acidic dissociation of the fluoroaquo-germanates should increase the equilibrium degree of hydrolysis of GeF₆²⁻. The pH of GeF₆²⁻ solutions which have been brought to hydrolytic equilibrium is also lower than that for equimolar SiF₆²⁻ solutions.

A number of conclusions can be drawn from these results relating to the attainment of hydrolytic equilibria in K₂GeF₆ solutions. In a strongly acidic medium, stepwise decomposition of GeF₆²⁻ occurs; we determined³ the equilibrium constant for the reaction

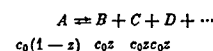


From this we calculated an approximate value for the equilibrium constant of the process



$K_{298} = 2 \times 10^{-4}$. If process (3) also predominated in aqueous K₂GeF₆ solutions, two particles of hydrolysis product would appear in the solution for every GeF₆²⁻ ion hydrolysed; actually the number is considerably higher.

Let us assume that species A decomposes in one stage into *n* species (B, C, D, etc.):



The equilibrium constant for the process is

$$K = (c_0z)^n / c_0(1-z)$$

or

$$\log[c_0(1-z)] = n \log[c_0z] - \log K. \quad (4)$$

If some of the species formed in the solution (for example B and C) are identical, this is reflected in the value of *K* (since their concentration should be equal to 2*c*₀*z*) but not in the value of *n*.

The dependence of log[c₀(1-z)] on log[c₀z] for K₂GeF₆ solutions, calculated from the data in Table 1, is shown in Fig. 2. The points for *z* ≥ 0.95 are not given, since for these points the error in the quantity log[c₀(1-z)] is very high. The broken straight lines in the right-hand side of the figure correspond to *n* = 2, 3, and 4.

The experimental results (Fig. 2) evidently do not correspond to the assumption that *n* = 2. Thus process (3) does not predominate and the [GeF₅(H₂O)]⁻ formed undergoes considerable further decomposition leading to an increase in the number of particles and a decrease in the pH of the solution. This is also indicated by the values of the observed degree of decomposition being much higher than those obtained when only equilibrium (3) is taken into account in the calculation. Moreover, if only equilibrium (3) applied, the pH of the solution would be greater than seven.

At 0° the dependence of log[c₀(1-z)] on log[c₀z] is given by a convex line whose slope lies between *n* = 3 and *n* = 4

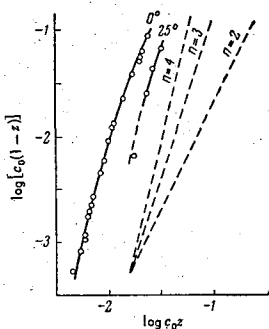
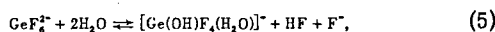
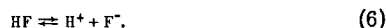


Fig. 2. Graphical analysis of the nature of the hydrolytic equilibrium for GeF_6^{2-} .

at higher concentrations and tends to $n = 4$ as the concentration falls. Since, moreover, the pH of the solution depends little on concentration, is close to the pK for the acidic dissociation of HF, and, like the latter quantity, increases with temperature, the experimental results are in keeping with the coexistence of two equilibria, which chiefly determine the composition of the solutions:

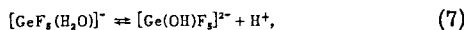


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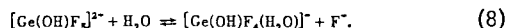


It must be assumed that $[\text{Ge}(\text{OH})\text{F}_4(\text{H}_2\text{O})]^-$ is a weaker Brønsted base than F^- .

Process (3) is apparently followed by the reactions



and



Since the replacement of F^- in GeF_6^{2-} by the more energetic donor OH^- should lead to an increase in the electron density on the germanium atom and a decrease in its acceptor properties, that is, a decrease in the strength of the bond between Ge and the fluorine atoms, and since the hydration energy of F^- is very high, the equilibrium constant for process (8) would be expected to be greater than that for process (3). In this case the equilibrium concentrations of $[\text{GeF}_5(\text{H}_2\text{O})]^-$ and $[\text{Ge}(\text{OH})\text{F}_5]^{2-}$ in dilute solutions should be low compared with the equilibrium concentrations of GeF_6^{2-} , $[\text{Ge}(\text{OH})\text{F}_4(\text{H}_2\text{O})]^-$, HF, and F^- , and the equilibrium conditions can be described satisfactorily by Eqn. (5), which is the sum of Eqns. (3), (7), and (8), with allowance for the equilibrium (6).

Attempts to account for the data on the basis of the stepwise character of processes (3), (7), (8), and (6), that is, by assuming the existence of appreciable concentrations of $[\text{GeF}_5(\text{H}_2\text{O})]^-$ and $[\text{Ge}(\text{OH})\text{F}_5]^{2-}$ in solution, led to conclusions which did not agree with the experimental data.

To confirm the accuracy of this assumption, we calculated approximate values for the equilibrium constant of process (5). Clearly the equilibrium concentrations of GeF_6^{2-} , $[\text{Ge}(\text{OH})\text{F}_4(\text{H}_2\text{O})]^-$, HF, and F^- are $c_0(1-z)$, c_0z , $c_0z(1-y)$, and $c_0z(1+y)$ respectively, where c_0 and z have the same significance as in Table 1 and y denotes the degree of dissociation of HF in an equimolar mixture of HF and F^- . The most recent value for K_{HF} at 25° was used

in the calculation of y . The value of K_{HF} extrapolated to 0°C is $K_{\text{HF}} = 1.06 \times 10^{-3}$. The calculated values of $1-y^2$ and

$$K_5 = c_0^2 \frac{z^3}{1-z} (1-y^2) \quad (9)$$

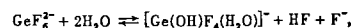
are given in Tables 1 and 2. The average values of z were used in the calculation of K_5 .

The values of K_5 calculated for 0° (Tables 1 and 2) vary only slightly, although the original fluorogermanate concentration varied from 11.21×10^{-3} to 0.21×10^{-3} , *i.e.* by a factor of more than 50. Since Eqn. (9) contains c_0 and z to high powers, the fact that the values of K_5 are constant confirms that the scheme of equilibria chosen is essentially correct. If we reject the values of K_5 from experiments 21-24, in which even a small error in the determination of z is very significant, the average value found for K_5 is $(1.2_3 \pm 0.2_5) \times 10^{-6}$.

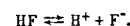
There are only a few data for 25° ; the value obtained in experiment 4 is clearly too high, and the average value of K_5 at 25° from experiments 1-3 is equal to $(5.2 \pm 0.3) \times 10^{-6}$. Application of the usual thermodynamic relationships for the temperature dependence of the equilibrium constant shows that reaction (5) is endothermic, with $\Delta H \approx 9.5 \pm 1.7$ kcal and $\Delta S_{298}^\circ \approx 8 \pm 6$ e.u.

SUMMARY

1. The equilibrium degree of hydrolysis and pH of K_2GeF_6 solutions with concentrations of 0.01121-0.00021 *m* at 0° and 0.010-0.00245 *m* at 25° have been measured.
2. The concentration dependence of the pH and degree of hydrolysis corresponds to the existence of the equilibria



and



3. The approximate values of the equilibrium constant for the first process at 0° and 25° are $(1.2_3 \pm 0.2_5) \times 10^{-6}$ and $(5.2 \pm 0.3) \times 10^{-6}$ respectively; the enthalpy and standard entropy of the process have the values $\Delta H = 9.5 \pm 1.7$ kcal and $\Delta S_{298}^\circ = 8 \pm 6$ e.u.

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