

Fig. 5. pH of solutions in the GeO_2 -aqueous hexamethylenetetramine solution system (1) and in the hexamethylenetetramine- H_2O system (2).

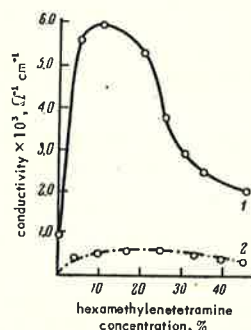


Fig. 6. Electrical conductivity of solutions in the GeO_2 -aqueous hexamethylenetetramine solutions system at 25°C (1) and in the hexamethylenetetramine- H_2O system (2).

The pH (Fig. 5) of pure hexamethylenetetramine solutions is much higher than that for solutions of germanium dioxide in hexamethylenetetramine, from which it follows that in this system, as in that containing ammonia, chemical reaction takes place between germanium dioxide and hydroxide ions, as a result of which the activity of the latter decreases considerably.

It was also found that the electrical conductivity of aqueous solutions containing GeO_2 and hexamethylenetetramine is many times greater than that of pure hexamethylenetetramine solutions with the same concentration (Fig. 6). This can be the case only if a compound which is more extensively dissociated than the original components is formed. Comparison of the GeO_2 - NH_3 - H_2O and GeO_2 -hexamethylenetetramine- H_2O systems shows that in the first system, where the ammonium hydroxide is a stronger base than hexamethylenetetramine, the ammonium germanate formed is more stable. The increased solubility of germanium dioxide in the presence of hexamethylenetetramine, the decrease in pH, and the increase in the conductivity of aqueous hexamethylenetetramine solutions in the presence of germanium dioxide definitely indicate the formation of a chemical compound, although this could not be isolated in the solid state.

SUMMARY

1. The germanium dioxide-aqueous ammonia solution system has been studied by solubility, electrical conductivity, and potentiometric methods at 25°C . The high solubility of germanium dioxide in aqueous solutions ($158.6 \text{ g GeO}_2 \text{ litre}^{-1}$ at $1.2\% \text{ NH}_3$) is due to the formation of ammonium germanate with composition $(\text{NH}_4)_3\text{HGe}_7\text{O}_{16}$. With increase in the ammonia concentration, the solubility of ammonium germanate decreases sharply and fine crystals with composition $(\text{NH}_4)_3\text{HGe}_7\text{O}_{16} \cdot 4\text{H}_2\text{O}$ are precipitated.
2. The solubility and electrical conductivity in the germanium dioxide-hexamethylenetetramine-water system have been studied. The solubility of germanium dioxide is increased, again due to the formation of germanate, but the compound formed with hexamethylenetetramine is less stable than ammonium germanate.

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Institute of General and Inorganic Chemistry, Academy of Sciences of the Ukrainian SSR

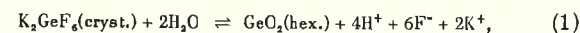
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OVERALL EQUILIBRIUM CONSTANT FOR HYDROLYSIS OF THE HEXAFLUOROGERMANATE ION GeF_6^{2-} AT 25°C

I. G. Ryss and N. F. Kulish

We determined the equilibrium constant of the process



at 25°C by potentiometric determination of the activities of the H^+ and F^- ions and measurement of the K^+ ion concentration in KF solutions of various concentrations, saturated with K_2GeF_6 and hexagonal (α -quartz type) GeO_2 . It can be seen that the equilibrium constant K_1 for process (1) is

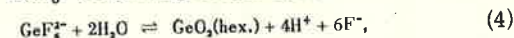
$$K_1 = [\text{H}^+]^4[\text{F}^-]^6[\text{K}^+]^2 = [\text{H}^+]^4[\text{F}^-]^6(\text{K}^+)^2\gamma_{\text{K}^+}^2. \quad (2)$$

Here and subsequently the square brackets denote the activities and the parentheses the concentrations of the given ions; γ is the activity coefficient.

The expression for the activity of saturated K_2GeF_6 solution:

$$[\text{K}_2\text{GeF}_6] = [\text{K}^+]^2[\text{GeF}_6^{2-}], \quad (3)$$

can be used to find the overall equilibrium constant for the hydrolysis of GeF_6^{2-} according to the equation



$$K = \frac{[\text{H}^+]^4[\text{F}^-]^6}{[\text{GeF}_6^{2-}]} = \frac{K_1}{[\text{K}_2\text{GeF}_6]}. \quad (5)$$

EXPERIMENTAL

Materials

To remove the traces of hydrogen carbonate ion from "chemically pure" grade KF, a 15% solution of the latter was heated with a slight excess of "chemically pure" grade KHF_2 , after which the cooled solution was neutralised exactly with carbonate-free KOH solution; the solution was evaporated until $\text{KF} \cdot 2\text{H}_2\text{O}$ crystallised on cooling, the crystals were washed with a small quantity of ice water, compressed, and dried between sheets of filter paper. K_2GeF_6 was purified by recrystallisation¹. GeO_2 containing 0.25% Cl, $1.2 \times 10^{-4}\%$ Si, and less than $10^{-5}\%$ Al, As, Mg, and Fe impurities was purified completely from traces of Cl^- by prolonged pyrohydrolysis². The X-ray powder diagram showed that the GeO_2 had the hexagonal structure.

PbF_2 was prepared by precipitation with NH_4F solution from a solution of "analytical reagent" grade lead acetate which had been further purified by recrystallisation from 1% acetic acid solution; the PbF_2 precipitate was washed with water acidified with HF, and dried in air. The $\text{KF} \cdot 2\text{H}_2\text{O}$ and PbF_2 were prepared only in polyethylene or platinum vessels. None of the reagents prepared contained detectable quantities of Cl^- , whose presence might have interfered in the action of the lead fluoride electrode.

Nitrogen, obtained by the reaction of sodium nitrite and ammonium sulphate solutions, was washed with acidic permanganate solution and stored in a gas holder filled with alkaline dithionite solution; the solution in the funnel of the gas holder and in the storage vessels was protected from atmospheric oxidation by a layer of oil.

Lead amalgam was prepared by the published method³ in an atmosphere of nitrogen from very highly pure mercury and lead which had been purified from traces of active metals and then redistilled in a vacuum (the lead was prepared by electrolysis at a mercury cathode with subsequent remelting in a high vacuum at 500°C).

Preparation of Specimens and Measurement Procedure

In the first series the equilibrium position was reached from the direction corresponding to hydrolysis of K_2GeF_6 . KF solutions with molality 0.08–0.5 were prepared by diluting (by weight) the original $\sim 1.562 \text{ m}$ solution. An excess of K_2GeF_6 , PbF_2 , and GeO_2 was added to the solutions in polyethylene vessels, and the mixtures were kept at constant temperature in a water thermostat with periodic agitation for 3.5 months at $25^\circ \pm 0.1^\circ$. This time interval ensured that the equilibrium state was reached, although the hydrolysis of GeF_6^{2-} in alkaline medium is relatively slow⁴.

In the specimens of the second series the equilibrium position was reached from the direction corresponding to the formation of K_2GeF_6 . $\sim 0.3 \text{ g}$ of HF solution containing

an equimolar quantity of KHF_2 was added to KF solutions saturated with GeO_2 , K_2GeF_6 , and PbF_2 , and containing an excess of the precipitates, in polyethylene vessels. The following reaction took place



These specimens were then brought to constant temperature under the conditions described above.

The presence of K_2GeF_6 and GeO_2 residues in the specimens before the measurement of the potentials was checked using a microscope. The solubility of GeO_2 in 1.5 m and saturated KF solution at 20° is lower than that in water ($\sim 0.03 \text{ m}$ and $\sim 0.026 \text{ m}$).

Measurements

Stable and reproducible results could not be obtained with a hydrogen electrode, so that the pH was measured with a quinhydrone electrode. It was established that GeO_2 does not influence the quinhydrone electrode in the pH range in which we were interested. The activity of the F^- ions was measured with a lead fluoride electrode^{5,6} containing a two-phase mixture of lead and PbF_2 precipitate. The reference electrode was a saturated calomel electrode connected to the circuit through an intermediate vessel containing saturated NH_4NO_3 solution, isolated by means of a No. 4 glass filter.

The cell (Fig. 1) was designed in such a way that there were no temperature differentials and that the solutions and electrodes were kept free from air by blowing nitrogen through all sections of the cell. After the cell had been filled with nitrogen, the solution being studied was introduced into vessel (1) together with the residues saturating it; some of the solution was forced into vessel (2). A stream of nitrogen was then blown through the solution and cell for 30 min [saturation of the N_2 with water vapour in vessel (2) prevented appreciable evaporation of the solution being studied] and it was forced into the cell, which was rinsed twice with the solution being studied. The solution was then transferred by suction into the lead fluoride electrodes[†] and the quinhydrone electrode, and the e.m.f. measurements were made. The temperature of the cell was kept constant at $25.00^\circ \pm 0.10^\circ$. The e.m.f. of the circuits was measured with a PPTV-1 potentiometer with LU-2 attachment. The e.m.f. values for the circuits of the quinhydrone and calomel electrodes were constant to within 0.2 mV; the difference in the potentials of the two lead fluoride electrodes changed with time by not more than several tenths of a millivolt, but the values in different measurements varied from several tenths of a millivolt to 8 mV; this was apparently due to the penetration of traces of oxygen into the electrodes while the latter were being filled. The e.m.f. of the lead fluoride electrode-calomel electrode circuits remained unchanged with time.

In the calculation of $\text{pF} = -\log[\text{F}^-]$ we used the published values of the standard potential of the lead fluoride electrode⁵ and the mean results obtained in the measurement of the e.m.f. values for both lead fluoride electrodes.

[†] After the solution had been transferred by suction into the lead fluoride electrodes, a mixture of solid K_2GeF_6 , GeO_2 , and PbF_2 was introduced into the electrodes [by rotating the vessels (6) connected by ground joints] to ensure that the solution remained saturated with all three solid phases.

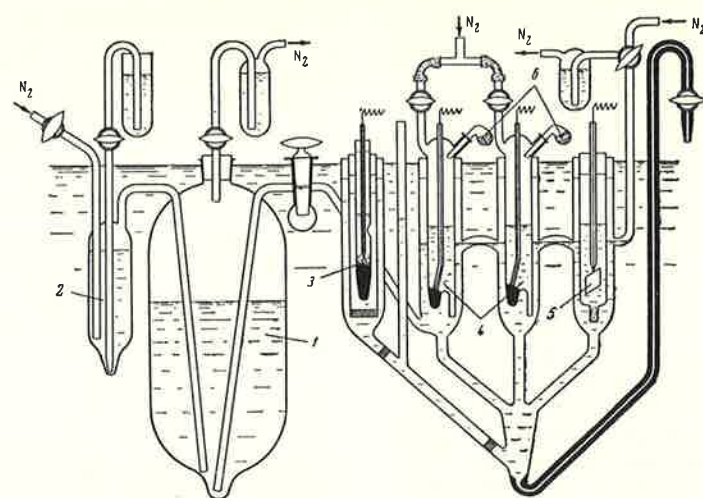


Fig. 1. Cell used to measure pH and pF:

1) vessel for solution being studied; 2) vessel for bringing the concentration of water vapour in the nitrogen to the equilibrium value above the solution being studied; 3) saturated calomel electrode; 4) lead fluoride electrodes; 5) quinhydrone electrode; 6) vessel containing a mixture of solid K_2GeF_6 , GeO_2 , and PbF_2 .

Potassium in the equilibrium solutions was determined gravimetrically as KBF_4 after evaporation with HBF_4 and HCl; repeated addition of HCl was necessary for the complete removal of germanium. Solutions with lower initial KF concentration (less than 0.03 m) contained appreciable quantities of dissolved PbF_2 ; before the precipitation of the potassium the solutions were diluted and the lead was removed by electrolysis on platinum electrodes. The results of the measurements are given in the Table.

DISCUSSION

The chief source of error in the determination of K_1 lies in the pF measurement; errors of ± 0.07 units in the determination of pF produce errors of ± 0.4 in the value of $\log K_1$. The salt error of the quinhydrone electrode in 0.5 m LiCl, KCl, or NaCl solutions is ~ 0.02 pH.⁷ It may be assumed that in ~ 0.5 m KF it has approximately the same value, which corresponds to an error of 0.08 in $\log K_1$. This error decreases with dilution of the KF solutions.

TABLE.

Initial KF concentration, m	Results of measurements				$-\log K_1$	Initial KF concentration, m	Results of measurements				$-\log K_1$					
	pF	pH	c_{K^+}				pF	pH	c_{K^+}							
Experiments of first series																
0.4996	0.614	6.71	0.4734	31.17	Mean 30.99	Experiments of second series										
0.2495	0.875	6.17	0.2506	31.13		0.4999	0.486	6.66	0.4945	30.17						
0.1248	1.37	5.33	0.1329	31.29		0.2500	0.880	6.10	0.2530	30.87						
0.0625	1.70	4.69	0.07546	31.20		0.1249	1.27	5.38	0.1337	30.89						
0.0313	1.94	4.19	0.05701	30.89		0.0623	1.67	4.73	0.07714	31.17						
0.0157	2.18	3.70	0.05066	30.47		0.0312	1.91	4.26	0.05873	30.92						
0.0078	2.36	3.48	0.04620	30.75		0.0154	2.14	3.79	0.05078	30.59						
						0.0079	2.38	3.47	0.04632	30.83						

The diffusion potentials, obtained by means of Henderson's equation⁸, were nearly zero in the most concentrated KF solutions; in the most dilute solutions they may exceed the pH or pF by ~ 0.02 .

Since it is difficult to estimate the activity coefficient of K^+ (particularly in solutions with low KF concentration, where the concentration of K_2GeF_6 and PbF_2 is higher), we took its value as equal to unity. Since the power of γ_{K^+} in the expression for K_1 is low, the error introduced in this way is small compared with that produced by the errors in the pF measurement.

Fig. 2 shows a plot of $(\log c_{K^+} - 2pH)$ against $3pF$. It follows from Eqn. (2) that in the equilibrium systems a straight line should be obtained, with slope of unity. The deviations from linearity in Fig. 2 are random, and not systematic, confirming that equilibrium was reached in the experiments of both series and that the results of the measurements contain no systematic errors. The mean value of $-\log K_1$ found from the experiments of the first series is 30.99 ± 0.30 (standard deviation); the experiments of the second series gave $-\log K_1 = 30.78 \pm 0.32$. The mean value from the two series is $\log K_1 = -30.88 \pm 0.3$, or $K_1 = (0.65-2.7) \times 10^{-31}$. The straight line in Fig. 2 is drawn through the ordinate corresponding to the mean value of $\log K_1$.

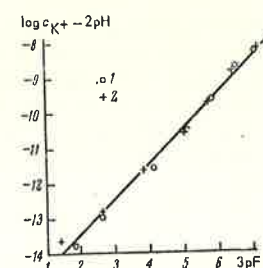
The solubility of K_2GeF_6 at 25° is $c = 0.0221$ m;⁹ this value shows good agreement with the value $c = 0.0223$ m.¹⁰

The degree of hydrolysis of GeF_6^{2-} in this solution is $\alpha = 0.20$.¹¹ Assuming that the mean activity coefficients of K_2GeF_6 and K_2SO_4 are equal (at the same molality), we find $\gamma_{\pm} = 0.629$.¹² Thus the activity of saturated K_2GeF_6 solution at 25° is

$$[K_2GeF_6]_{sat} = 4c^2(1-\alpha)^2 = 4 \times (0.0221)^2 \times 0.8 \times (0.629)^2 = 8.6 \times 10^{-6}$$

Substituting this value in Eqn. (5), we find that at 25°

$$\log K = -25.81 \pm 0.3; \quad K = (0.76-3.2) \times 10^{-26}$$

Fig. 2. Dependence of $\log c_{K^+} - 2pH$ on $3pF$.

which is only slightly greater than the overall constant for the hydrolysis of SiF_6^{2-} .¹³

The standard free energy of reaction (4) is

$$\Delta F_{298}^\circ = -RT \ln K = 35.2 \pm 0.4 \text{ kcal.}$$

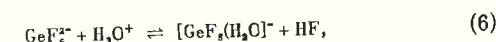
Using the published value of ΔF_{298}° for hexagonal GeO_2 ¹⁴ and the tabulated data for ΔF_{298}° for the other substances taking part in the reaction¹⁵, we calculated the standard free energy of formation of dissolved GeF_6^{2-} at 25° :

$$\Delta F_f^\circ = -438.0 \pm 1.5 \text{ kcal.}$$

We previously determined the equilibrium constants for the hydrolysis of GeF_6^{2-} to $[GeF_5(H_2O)]^-$ and to $[Ge(OH)F_4(H_2O)]^-$.¹¹ The determination of ΔF_f° for GeF_6^{2-} makes it possible to calculate ΔF_f° for these complexes; the values found (accuracy ± 2 kcal) are respectively -424 kcal and -408 kcal.

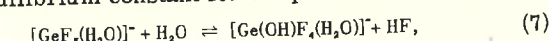
The value of ΔF_f° for undissociated aqueous HF, which is required for the calculations and is not given in reference books¹⁵, can be calculated from $\Delta H^\circ = -3.18$ kcal¹⁶ and the dissociation constant $K = 6.71 \times 10^{-4}$ ¹⁷ for the dissociation of aqueous HF to form ions at 25° . The free energy of formation of undissociated aqueous HF at 25° is -70.41 kcal.

A recent paper by Benoit and Place¹⁸ described a study of the formation of fluorogermanates by methods involving the extraction of germanium with carbon tetrachloride and determination of the activity of F^- with an iron(II)-iron(III) electrode. Benoit and Place did not make allowance for the existence of fluoroaquo germanates in the solutions but it can be shown that this has no influence on the determination of the mean ratio $\bar{i} = F/Ge$ in the complexes. The mean value which they found for \bar{i} in the complexes does not exceed 5. In the extraction experiments they used 8.12-11.12 m HCl, and HF concentrations not exceeding ~ 0.5 m. Since the acidity h_0 of 6 m HCl is 132, and that of 10 m HCl is 4800,¹⁹ and the equilibrium constant for the process



is 0.29,¹ it can readily be seen that the equilibrium ratio of the concentrations of GeF_6^{2-} and $[GeF_5(H_2O)]^-$ in these conditions must be negligible. In the potentiometric determination of \bar{i} , Benoit and Place used solutions with $(H^+) = 0.50$ M and an HF concentration not exceeding 0.04 M; our data indicate that in these conditions the ratio of the concentrations of GeF_6^{2-} and $[GeF_5(H_2O)]^-$ may reach ~ 0.275 , which corresponds to $\bar{i} = 5.2$. Under these conditions, however, considerable hydrolysis of $[GeF_5(H_2O)]^-$ to $[Ge(OH)F_4(H_2O)]^-$ and possibly to $[GeF_4(H_2O)_2]$ may occur, leading to a significant decrease in \bar{i} .

The equilibrium constant for the process



calculated from our data^{1,11}, is $\sim 2 \times 10^{-2}$. At $[HF] = 0.04$ M, the ratio of the concentrations of $[Ge(OH)F_4(H_2O)]^-$ and $[GeF_5(H_2O)]^-$ is ~ 0.5 and the corresponding value of \bar{i} is ~ 4.67 . For the formation of $[GeF_4(H_2O)_2]$, which is possible in strongly acidic solutions, \bar{i} undergoes a further decrease.

The method used by Benoit and Place did not make it possible to detect GeF_6^{2-} in the solution. We obtained reliable evidence for the existence of GeF_6^{2-} in the solutions by studying not only the equilibria but also the kinetics of the processes^{2,4}; thus Fig. 5 in the paper by Benoit and Place, showing the ratio of the quantities of the different forms of fluorogermanate, is not correct.

Benoit and Place calculated the ratios

$$\beta'_5 = \frac{\sum_{j=N-1} (Ge(OH)_j F_j)}{(GeO_2)(HF)^5} = (8.8 \pm 0.2) \times 10^8,$$

$$\beta'_4 = \frac{\sum_{j=N-1} (Ge(OH)_j F_j)}{(GeO_2)(HF)^4} = (2.0 \pm 0.3) \times 10^7.$$

The numerical values of β'_5 and β'_4 relate to $[H^+] = 0.5$ M.

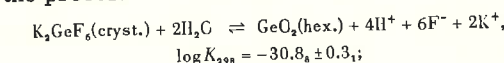
The numerators of these ratios contain the sums of the concentrations of all forms of fluorogermanate containing respectively five or four F atoms per Ge atom. If it is assumed that the predominant forms are $[GeF_5(H_2O)]^-$ and $[Ge(OH)F_4(H_2O)]^-$, the ratio β'_4/β'_5 should be close to the constant for equilibrium (7). In actual fact, $\beta'_4/\beta'_5 \approx 2.3 \times 10^{-2}$. The agreement with the above value is better than might have been expected.

With the same assumption, we can calculate the value of β'_5 from the values which we have obtained for the constants for equilibria (4) and (6), the dissociation constant of HF, and the solubility of GeO_2 . Using for the latter the published value $s = 4.33 \times 10^{-2}$ M,²⁰ we obtain $\beta'_5 = 0.80 \times 10^8$, which differs from that found by Benoit and Place by less than one order of magnitude; the same discrepancy is observed in the case of the values of β'_4 .

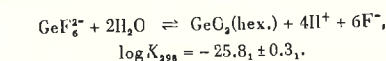
SUMMARY

1. Measurements of the pH, pF, and K^+ ion concentrations in solutions saturated with K_2GeF_6 and GeO_2 at 25° have been used to obtain the following equilibrium constants:

for the process



for the process



2. The standard free energies of formation of the ions GeF_6^{2-} , $[GeF_5(H_2O)]^-$, and $[Ge(OH)F_4(H_2O)]^-$ have been calculated. The equilibria in fluorogermanate solutions have been discussed. It has been shown that Benoit and Place¹⁸ could not detect the existence of GeF_6^{2-} in solution with the procedure and conditions which they used. The

