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presence of a hydrogen bond. The bands at 1780 and 1460 cm^{-1} are shifted towards lower wavenumbers by 90 and 100 cm^{-1} respectively; this confirms the solvation of the fluorides.

These investigations show that CF_3COOH is a promising reagent for preparing anhydrous fluorides of alkaline-earth metals and lanthanides. A method for preparing anhydrous lanthanide fluorides in a highly pure finely crystalline state has been developed.

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Investigation of the Solubility of Germanium Dioxide in Water at 25–300 °C

T.B.Kosova, L.N.Dem'yanets, and T.G.Uvarova

The solubility of two polymorphic modifications of GeO_2 in water at 25–300 °C has been investigated. The solubility of $\text{GeO}_2(\text{hex})$ at temperatures above 100 °C cannot be determined experimentally. The solubility of $\text{GeO}_2(\text{tetr})$ varies from 3×10^{-5} to $1.7 \times 10^{-2}\text{M}$ as the temperature is raised from 50° to 300 °C. The solubility of $\text{GeO}_2(\text{tetr})$ in water in the pH range 2–9 is independent of the pH, the germanium dissolving as the neutral complex, $\text{Ge}(\text{OH})_4^0$.

Crystalline germanium dioxide can exist in three polymorphic modifications, with structures of the rutile, α -quartz, and α -cristobalite types.^{1–3} The low-temperature tetragonal modification with a rutile structure is stable up to 1035 °C at 1 atm (1308 K at 0.1 MPa). Under normal conditions the tetragonal (as stable) and the hexagonal (as metastable) modifications can coexist; the solubility of the latter [of the two? (Ed.of Translation)] should, under these conditions, significantly exceed the solubility of the rutile-like form. In the presence of H_2O the metastable modification $\text{GeO}_2(\text{hex})$ is converted into the stable $\text{GeO}_2(\text{tetr})$, according to published data for 180 °C.¹ The third modification of

GeO_2 —tetragonal with a low-temperature cristobalite structure—was observed comparatively recently;^{3,4} its stability region has not been determined.

The solubility of the tetragonal modification of GeO_2 in water at room temperature had been studied in detail earlier by many investigators. An analysis of these published results and a summary graph of the dependence of the solubility on pH of the solutions at 25 °C were given by Kossova and co-workers.⁵ We note that the solubilities of $\text{GeO}_2(\text{hex})$ in water at 25 °C given by various investigators varied between 0.039 and 0.048 m. The solubility of $\text{GeO}_2(\text{amorph})$ was somewhat higher than that of $\text{GeO}_2(\text{hex})$ and amounts to $5.1 \times 10^{-2}\text{M}$ at 100 °C.⁶ The solubility of $\text{GeO}_2(\text{tetr})$ at 25 °C was almost three orders of magnitude less than that of $\text{GeO}_2(\text{tetr})$ and amounts to $4.5 \times 10^{-5}\text{M}$. The solubility of the cristobalite form has not been investigated; this modification was not obtained pure and always contains $\text{GeO}_2(\text{hex})$ as impurity.

According to the literature, the solubility of the hexagonal modification of GeO_2 in H_2O increases linearly with the temperature, reaching $1.4 \times 10^{-1}\text{M}$ at 100 °C.⁷ Results on the behaviour of the tetragonal modification of GeO_2 in water at elevated temperatures are absent from the literature.

We have studied experimentally the solubility in water of the tetragonal modification of GeO_2 with a rutile type of structure at temperatures of 25–300 °C, and pressures from saturated vapour pressure to 140 MPa; we also investigated the behaviour of $\text{GeO}_2(\text{hex})$ in water at $t \geq 100\text{ °C}$.

EXPERIMENTAL

The solubility of $\text{GeO}_2(\text{tetr})$ in water was determined by quenching saturated solutions and analysing specimens of the solution. In this instance the quenching method can be used since dissolving $\text{GeO}_2(\text{tetr})$ gives solutions which are stable at room temperature for a long period: we did not observe any change in the GeO_2 concentration in the solution obtained by quenching from 300 °C to room temperature when it was stored for three months.

Table 1. Solubility of $\text{GeO}_2(\text{hex})$ in water.

$t, \text{ °C}$	$T, \text{ K}$	Mass, %	$\text{GeO}_2, \text{ M}$	$\lg m_{\text{GeO}_2}$	$\lg m_{\text{GeO}_2}(\text{calc})$
0	273.15	0.27	$2.3 \cdot 10^{-3}$	-1.5882	-1.6309
25	296.15	0.50	$4.3 \cdot 10^{-2}$	-1.3206	-1.3701
50	323.15	0.75	$6.8 \cdot 10^{-2}$	-1.1445	-1.1676
75	348.15	0.98	$1.0 \cdot 10^{-1}$	-1.0283	-0.9943
100	373.15	1.19	$1.4 \cdot 10^{-1}$	-0.9440	-0.8480

Experiments to determine the solubility at $t > 100\text{ °C}$ were carried out in autoclaves of $\sim 40\text{ cm}^3$ volume, made of 45KhMnFA steel and lined with silver. The treatment time was 6–20 h, depending on the experimental temperature. Quenching to room temperature was carried out in flowing water for 5–10 min. At $t < 100\text{ °C}$, the experiments were carried out in sealed boxes made of SF-4 fluoroplastic in an oil thermostat.

After quenching, specimens of the solution were withdrawn for analysis to determine the GeO_2 concentration and measure the pH of the solution (R-340 potentiometer).

The germanium concentration in the solution was determined photocolometrically with phenylfluorone. The relative error in the determination of Ge in the solution was 10–15%, the sensitivity of the method 0.08 μg ml⁻¹.

To determine the solubility of GeO₂(hex) we used "special purity" grade reagents; to determine the solubility of GeO₂(tetr) we used the tetragonal modification of germanium oxide which we had made by treating "special purity" grade GeO₂(hex) with water at 190–450 °C in autoclaves of capacity 0.5–1.0 litre with silver or Teflon linings. Triply-distilled water (pH 6.8) was used for the experiments. Doubly-distilled water (pH 6.3 or 5.7) was also used in the experiments at t = 50 °C. Equilibrium was usually approached "from beneath"; in several instances, on approaching equilibrium "from above" we used the hexagonal modification of GeO₂.

The time for maintaining the conditions was determined experimentally; it was from 6 to 45 d at 300° and 100 °C and up to a year at 25° and 50 °C. The solid phase was identified at the end of an experiment by X-ray powder diffraction with λ₁ Cu Kα radiation.

RESULTS AND DISCUSSION

The experiments to determine the solubility of GeO₂(hex) in H₂O at t > 100 °C showed that the obtainable Ge concentrations could not be considered as the solubility of GeO₂(hex), since in experiments lasting more than 30 d the solid phase showed signs of the presence of stable tetragonal modification of GeO₂. The amount of GeO₂(tetr) increases with the duration of the experiment. This suggests that the transformation temperature of 180 °C given in the literature is tentative and the transformation of GeO₂(hex) into stable modification GeO₂(tetr) is determined by the kinetics of the process.

Treatment of the published data⁷ on the solubility of GeO₂(hex) in water at the temperatures in the range 25 to 100 °C (Table 1) gives the equation:

$$\lg m_{\text{GeO}_2} = -767/T + 1.207 \quad (1)$$

This relationship is plotted in the Figure (curve 1). In investigating the solubility of GeO₂(hex) the solid phase after the experiment was always found to be the tetragonal modification of GeO₂. As the experiments showed, the determination of the solubility of GeO₂(tetr) depend significantly on the synthesis conditions for the GeO₂(tetr) used in the experiment. The lower the synthesis temperature for the GeO₂(tetr), the higher the experimentally determinable solubility of this material at elevated temperatures for τ = const. Thus for GeO₂(tetr) synthesised at 190 °C, the solubility at 300 °C is 2.5 × 10⁻² m, whereas for GeO₂(tetr) obtained at 400 °C the corresponding value is 1.7 × 10⁻² m, the time of holding under these conditions being 6 d in both instances. Such a scatter in the experimental values can be explained in two ways: a change in the dispersion of the synthesised GeO₂ and a change in its rate of dissolving in water; or by a change in the fraction of GeO₂(hex) in the GeO₂(tetr) specimens obtained at different temperatures. The X-ray diffraction patterns of GeO₂(tetr) synthesised at different temperatures differ insignificantly in the half-widths of the main diffraction peaks: the lower the synthesis temperature, the greater the half-width of the peaks. On the diffraction patterns of the initial specimens of GeO₂(tetr) the lines of GeO₂(hex) are not recorded, consequently <5% of GeO₂(hex) is present in these specimens. A reflection of the presence of GeO₂(hex) in the initial material is the increase in the solubility of the GeO₂(tetr).

The results of determining the solubility of GeO₂(tetr) are given in Table 2. Each value given for the solubility is the mean of at least two parallel determinations of Ge in the solution.

The determination of the solubility of GeO₂(tetr) in water at room temperature is considerably more difficult because of the slow equilibration and the very low solubility. The experimentally determined solubility is 4 × 10⁻⁶ M, which is approximately an order of magnitude below the solubility given by Müller.⁶

The solubility of GeO₂(tetr) increases from 3.8 × 10⁻⁴ to 1.7 × 10⁻² M as the temperature is raised from 100 to 300 °C.

When GeO₂(hex) is used as the initial material, equilibrium is approached "from above".

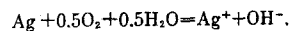
Table 2. Solubility of GeO₂(tetr) in water.

t, °C	Filling coefficient	Time, d	pH		Solubility		
			initial	after expt.	mass %	\bar{m}	$\lg \bar{m}$
25	0.95	150	2	2	6.2·10 ⁻⁵	(4.5±2.8)·10 ⁻⁶	-5.34
	0.95	150	6.4	6.3	4.9·10 ⁻⁵		
	0.95	150	2	2	6.9·10 ⁻⁵		
	0.95	240	2	2	3.5·10 ⁻⁵		
	0.95	240	2	2	1.2·10 ⁻⁵		
50	0.95	22	2	2	4.2·10 ⁻⁴	(2.8±0.9)·10 ⁻⁵	-4.54
	0.95	22	2	2	3.2·10 ⁻⁴		
	0.95	150	2	2	3.0·10 ⁻⁴		
	0.95	150	5.7	5.7	2.8·10 ⁻⁴		
	0.95	180	2	2	2.0·10 ⁻⁴		
100	0.95	45	6.8	8.9	3.8·10 ⁻³	(3.8±1.2)·10 ⁻⁴	-3.42
	0.95	45	6.8	7.6	3.4·10 ⁻³		
	0.95	45	6.9	9	4.8·10 ⁻³		
	0.95	28	6.8	9	2.1·10 ⁻³		
	0.95	28	6.8	9.3	3.6·10 ⁻³		
160	0.95	15	6.8	9.3	3.6·10 ⁻³	-	-2.60
	0.95	15	6.8	8.9	6.6·10 ⁻³		
	0.95	15	-	-	2.3·10 ⁻³		
	0.95	23	6.8	9.5	2.6·10 ⁻²		
	0.95	23	6.8	9.5	2.6·10 ⁻²		
190	0.80*	30	6.8	2.4	4.5·10 ⁻²	(4.4±1.3)·10 ⁻³	-2.35
	0.90	9	6.8	9.2	4.8·10 ⁻²		
250	0.80*	30	6.8	2.3	1.2·10 ⁻¹	(1.1±0.2)·10 ⁻²	-1.96
	0.90	6	6.8	7.8	1.2·10 ⁻¹		
	0.80	6	6.8	9.8	1.0·10 ⁻¹		
300	0.90	11	6.8	9.5	1.8·10 ⁻¹	(1.7±0.3)·10 ⁻²	-1.77
	0.75	6	6.8	7.9	1.8·10 ⁻¹		
	0.85	4	6.8	-	1.5·10 ⁻¹		
	0.75*	12	6.8	-	2.0·10 ⁻¹		
	0.80	5	6.8	8.2	1.6·10 ⁻¹		

*Approach to equilibrium "from above".

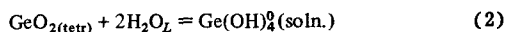
Under these circumstances the solution is found to be acidified after the experiment, the pH of the solution had fallen to 2.3–2.4 (Table 2). The decrease in pH is due to the GeO₂(hex) being used having been obtained by hydrolysis of GeCl₄. When such a reagent dissolves it gives an acid reaction. In every other instance [starting material: GeO₂(tetr)] the pH after the experiment varied between 7.6 and 9.3.

Some increase in the pH of the solution (initial pH = 6.8) can be attributed to the oxidation of the material of the Ag lining by oxygen present in the autoclave. The oxidation leads to an increase in the concentration of OH⁻ according to the reaction:



For a filling coefficient of 0.7–0.9, oxygen remaining in the free space of the autoclave is sufficient to raise the pH to ~9; the greatest OH⁻-ion concentration in the solution after quenching did not exceed 10⁻⁵ (pH ~9).

Although the pH of the solution varied within the range 2–9, the solubility of $\text{GeO}_2(\text{hex})$ remained almost constant. The lack of dependence of the solubility of $\text{GeO}_2(\text{tetr})$ on the pH at constant temperature shows that germanium is transferred into a solution predominantly as neutral species. Then the reaction in which $\text{GeO}_2(\text{tetr})$ dissolves in water can be written as:

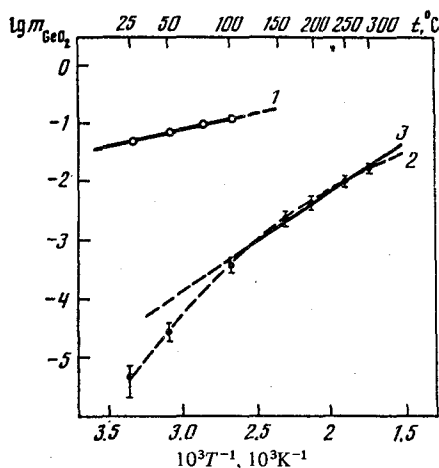


The low absolute magnitudes of the solubility of $\text{GeO}_2(\text{tetr})$ and the high temperatures of the experiment, which facilitate the depolymerisation, suggest that in the test solutions at high temperatures germanium polynuclear hydroxo-complexes are absent.

The experimental data obtained on the solubility of $\text{GeO}_2(\text{tetra})$ throughout the temperature range investigated (25–300 °C) (cf. Figure, curve 2) are described by the equation:

$$\lg m_{\text{Ge}(\text{OH})_4^0} = -4132/T + 11.969 - 0.011559T, \quad (3)$$

that is, for dissolving germanium dioxide in water $\Delta C_p \neq 0$.



Variation of the solubility of the polymorphic modifications of GeO_2 in water with the temperature. Curves 1–3 are explained in the text.

Nevertheless the low solubilities at 25° and 50 °C and the difficulty of reaching equilibrium for $\text{GeO}_2(\text{tetr})-\text{H}_2\text{O}$ at these temperatures does not rule out possible errors in the determination of the solubility of $\text{GeO}_2(\text{tetr})$ under these conditions. Data on solubility at the higher temperatures must be considered to be the most reliable, the temperature dependence of the solubility in the range 100–300 °C being almost linear (Figure, curve 3) and can be described by the equation:

$$\lg m_{\text{Ge}(\text{OH})_4^0} = -1774/T + 1.403 \quad (4)$$

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Aqueous-salt Systems Containing Lanthanide Nitrates and Hydrazinium Mononitrate

D.A.Khisavea

Solubility in the systems $\text{Ln}(\text{NO}_3)_3-\text{N}_2\text{H}_4\cdot\text{HNO}_3-\text{H}_2\text{O}$, where Ln = Sm, Gd, or Dy, has been measured at 25° and 50 °C. There is no reaction between the component salts in any of these systems.

This work is a continuation of studies of the reaction between lanthanide nitrates and hydrazinium mononitrate in aqueous solution.^{1–4} Since, other conditions being equal, the coordinating ability of the central lanthanide ion is influenced by the nature of this ion, it is advisable to examine these relationships for other representatives of this group of metals. Experimental data on the solubility of the solid phases in the systems quoted in the Abstract are therefore presented.

EXPERIMENTAL

The solubility was studied at 25° and 50 °C by means of sections.⁵ The refractive index of the liquid phase was measured for mixtures of the components situated on strictly aligned sections of the concentration triangle of the system. The compositions of the saturated solutions and the corresponding equilibrium solid phases were found graphically from the points at which there are breaks on the curves showing the property as a function of composition. In all three systems ten sections in the composition triangle were used. Five of these sections run from the amine salt corner to the $\text{H}_2\text{O}-\text{Ln}(\text{NO}_3)_3$ side and the others spread out fanwise from the point with the composition $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ to the opposite side.

The samarium, gadolinium, and dysprosium nitrates used were obtained by recrystallising the crystalline hydrates of the respective "chemically pure" grade lanthanide nitrates.