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i.r. spectra at *ca.* 800 cm^{-1} (Fig.1b). The X-ray diffraction patterns of specimens containing up to 33 mole % La_2O_3 show reflections belonging to the niobate and also to niobium(II) oxide which is formed by the disproportionation of niobium(IV) oxide. Reflections due to niobium(IV) oxide appear up to 25 mole % La_2O_3. The pyrochlore phase is present in the X-ray diffraction patterns starting with the specimens having 20 mole % La_2O_3. The lattice parameters of $La_2Nb_2O_7$ are similar in both the La_2O_3-NbO and $La_2O_3-NbO_2$ systems. The possible presence of $La_2Nb_2O_7$ in specimens with compositions in the range 20–50 mole % La_2O_3 is indicated by the splitting of the band at *ca.* 580 cm^{-1} and the reduction in the intensity of the band at *ca.* 790 cm^{-1} in their i.r. spectra.

The X-ray phase analysis does not register the formation of $LaNb_3O_9$ but its presence is indicated by a band at *ca.* 915 cm^{-1} in the spectra of specimens containing more than 60 mole % La_2O_3.

The curve showing the dependence of the electrical resistivity on the composition of the specimens from the $La_2O_3-NbO_2$ system is complex (Fig.2b), like that for the La_2O_3-NbO system, owing to *the large number of phases involved. An increase in the amounts of* $LaNbO_4$ and La_2O_3, which possess dielectric properties, leads to an increase in the electrical resistivity, while the appearance of the $La_2.Nb_2O_7$ phase leads to a decrease.

Thermogravimetric analysis of specimens from the two systems showed that oxidation takes place in a single stage irrespective of the composition of the specimen and is indicated by an exothermic effect at 400 –440 °C.

This study of the phase equilibria in the La_2O_3-NbO and $La_2O_3-NbO_2$ systems thus shows that in all cases disproportionation of the niobium oxides is observed on the addition of even small quantities of lanthanum oxide. The higher oxide of niobium cannot coexist at high temperatures in the presence of niobium metal but the occurrence in the specimens of a lanthanum niobate containing the niobium(IV) cation can be explained by a dynamic equilibrium between the following phases:

$$LaNbO_4+Nb(NbO)\rightleftharpoons La_2Nb_2O_7,$$

this equilibrium being displaced to the left.

$La_2Nb_2O_7$ will thus exist over a wide concentration range but in many of the *specimens it is not detected owing to its low concen*tration.

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Behaviour of Germanium Dioxide in Water and Aqueous Solutions at Temperatures of 25-300 °C

T.B.Kosova and L.N.Dem'yanets

The state of germanium in water and in aqueous solutions of electrolytes over a wide range of temperatures (25–300 °C) and pH of the solution (1–14) has been investigated. The dissolution of $GeO_{2\,hex}$ at pH 1–8 takes place with the formation of neutral, predominantly mononuclear species. At pH $<$ 1 cationic forms of Ge are absent from the solution; at pH $>$ 9, the stable solid phases are alkali metal or ammonium germanates. An equation for the experimental temperature dependence of ΔG_T^0 for the $GeO_{2\,tetr}-GeO_{2\,hex}$ transformation and the theoretical temperature dependence of the solubility of the metastable hexagonal modification of GeO_2 in water have been calculated. Fields for the predominance of the germanium hydroxo-complexes in the solutions at 25–300 °C and pH 5–12 have been deduced. The thermodynamic properties of hydroxo-complexes $Ge(OH)_4^0$ and $GeO(OH)_3^-$ in aqueous solution at 25–300 °C are derived.

Three polymorphic modifications of crystalline germanium dioxide are known: the low-temperature modification with a rutile structure ($GeO_{2\,tetr}$), the high-temperature modification with an α-quartz structure ($GeO_{2\,hex}$), and a third (tetragonal) modification with a low-temperature cristobalite structure, the stability region of which has not been determined. The $GeO_{2\,tetr}-GeO_{2\,hex}$ transformation temperature is 1035 °C at 0.1 MPa.[1-3] Under normal conditions there are just two modifications: tetragonal (stable) and hexagonal (metastable).

There have been many investigations of the solubility and behaviour of GeO_2 in water and aqueous solutions of acids and alkalis at room temperature, but data on the state of GeO_2 in aqueous media are somewhat inconsistent. A critical analysis of the published information and the results of our investigations are given below.

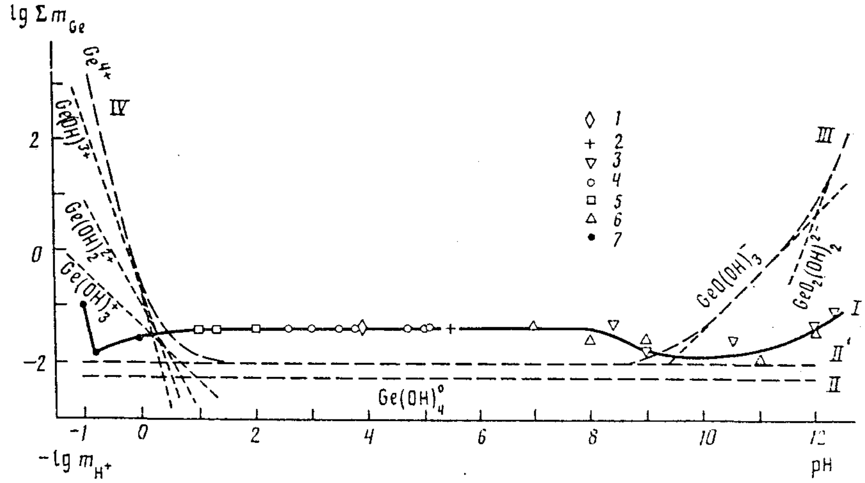

Figure 1. Solublility of $GeO_{2\,hex}$ in water and in aqueous solutions of electrolytes at 25 °C. (I) Solubility curve from published data. (1) Ref.4; (2) Ref.6; (3) Ref.7; (4) Ref.8; (5) Ref.9; (6) Ref.11; (7) Ref.12; (II) and (II′) boundary of existence of monomers according to published data;[13,10] (III) metastable equilibrium GeO_2-H_2O in the presence of alkali metal germanates; (IV) solubility curve of $GeO_{2\,hex}$ at pH < 1 on assuming that cationic species of germanium are present.

Solubility of GeO_2 in Water and Aqueous Solutions at Room Temperature.†

The solubility of GeO_2 in water at 25 °C varies from 0.039 to 0.048m.‡ An analysis of the results shows that the pH values of the saturated (in relation to $GeO_{2\,hex}$) solutions differ significantly. The dissolution of $GeO_{2\,hex}$, prepared by the hydrolysis of $GeCl_4$, gives a weakly acid reaction with pH from 3.9 to 5.4.[6] A solution of GeO_2 obtained by neutralising solutions of sodium germanate has a weakly alkaline reaction with pH 8.42.[7] Hence, the pH of the solution obtained by dissolving GeO_2 in water depends on the method of preparation of the germanium dioxide. The absolute magnitude of the solubility in every instance is practically identical: 0.042–0.048m.

Published data[4–17] from previous experimental investigations of the solubility of $GeO_{2\,hex}$ in water and in aqueous solutions at 25 °C were reduced by us to a single $\lg \varepsilon m_{Ge}$ scale and are plotted in Fig.1 as a function of pH. The form of curve 1 in the pH range 1–8 shows the variation of the solubility with the pH of this solution, which is evidence of the predominance under these conditions of non-charged germanium-containing species.

The experimental solubility of $GeO_{2\,hex}$ decreases both in strongly acidic (pH < 1), and in alkaline (pH > 8–9) solutions. As the concentration of alkali is raised the solubility of the GeO_2 falls to a minimum of 0.0171m ($\lg m = -1.77$) at pH = 9.07 [7] and then rises when the pH is increased further. According to Gayer[7] this increase in solubility is due to the formation of the complexes $GeO\cdot(OH)_3^-$ and $GeO_2(OH)_2^{2-}$. However, it has been shown in a series of studies[11,12] that at pH 8.5–9 the equilibrium solid phases are the polygermanates $Na_2Ge_5O_{11}.nH_2O$, $Na_2Ge_5O_{11}$, and $Na_2Ge_4O_9$, the compositions of which vary as the alkali concentration is increased. Analogous results were obtained in studying the solubility of $GeO_{2\,hex}$ in solutions of other alkalis. Thus, in NH_4OH solutions with concentrations > 0.3m in equilibrium with the solution are ammonium germanates, the solubility of which increases with the NH_4OH concentration.[5] Hence, curve *1* (Fig.1) at pH values > 9 corresponds to the solubility of the corresponding polygermanates and not GeO_2. Consequently, the experiments which Gayer[7] carried out must relate to the sodium germanate–water system and the constants he determined cannot be considered as equilibrium constants for the formation of $GeO(OH)_3^-$ and $GeO_2(OH)_2^{2-}$. An analogous change in the solubility of $GeO_{2\,hex}$ is observed in strongly acidic solutions (pH < 1) on increasing the acid concentration. An experimental investigation of solutions of hydrohalic acids[12,14–19] showed that the $GeO_{2\,hex}$ has a minimum solubility at an acid concentration of 4–6m; a further increase in concentration brings about an increase in the $GeO_{2\,hex}$ solubility. This rise in solubility was linked by Knyazev[15] and Pugh[16] with the formation of complexes of the type:

$$Ge(OH)_xCl_{6-x}^{2-}\quad Ge(OH)_xCl_{5-x}^{-},$$

at HCl concentrations > 8m a new solid phase was observed: $GeCl_4$.[14] Hence, the strongly acidic region does not comprise the "pure" GeO_2-H_2O system.

Forms in Which Germanium is Found in Solution

The predominance of one or another form of germanium in solution in the absence of a complex-forming agent (and also of several other cations, such as Si, Al, Sn) determines the total concentration Σm_{Ge}, the coordination number of the germanium in the solution, the $H^+(OH^-)$ concentrations, and the temperature of the solution.

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†The equilibrium reached when studying the solubility of $GeO_{2\,hex}$ is metastable, since the stable solid phase is the rutile-like modification of GeO_2. In our experiments, the solid phase observed in equilibirum with the solution, even after keeping for long periods (20–30 d) at 100 °C, was $GeO_{2\,tetr}$ rather than $GeO_{2\,hex}$.

‡m denotes the number of moles of solute per 1000 g H_2O.

Despite the large number of papers describing investigations of the behaviour of germanium dioxide in water and aqueous solutions,[2] consistent results on the form of germanium in these solutions have not been achieved.

At low germanium concentrations ($\Sigma m_{Ge} < 0.005\, m$ [13] or $\Sigma m_{Ge} < 0.01m$ [10,13]) and in the absence of complex forming anions of the type F^-, Cl^-, etc., monomeric germanium-containing species predominate. In neutral and alkaline solutions (pH 7–13) they are monomers of the type $Ge(OH)_4^0$, $GeO(OH)_3^-$, $GeO_2(OH)_2^{2-}$.[13,21] When the germanium concentration in the solutions exceeds $0.005m$ ($0.01m$), polynuclear species appear, the fractions of which increase with increase in the germanium concentration in the solution. The poly-ions can have the compositions: $H_2Ge_5O_{11}$ and its dissociation products, $HGe_5O_{11}^-$ and $Ge_5O_{11}^{2-}$,[10,19,22] $HGe_7O_{16}^{3-}$,[22] and $\{[Ge(OH)_4]_8.(OH)_3\}^{3-}$.[13] The degree of polymerisation of the germanium species depends on the germanium concentration and the pH of the solution. The formation of the poly-ions has been shown experimentally for pH > 7 at $m_{Ge} \geqslant 0.005m$.[13,21] The polymerisation factor in nearly neutral and weakly alkaline solutions is 5–8.[10,13] A further increase in alkalinity leads to decomposition of the polymers to form the monomers $GeO(OH)_3^-$ and $GeO_2(OH)_2^{2-}$.[13,22,23]

The ratio of the monomers and polymers in the equilibrium GeO_2-saturated solutions can be determined from the dissociation constants of the polymeric species. The equilibrium constant of the formation reactions of the poly-ions $\{[Ge(OH)_4]_8(OH)_3\}^{3-}$ was found by Ingri:[13,21]

$$8Ge(OH)_4{}^0+3OH^-=\{[Ge(OH)_4]_8(OH)_3\}^{3-};\quad \lg K=29.14\pm0.5 \tag{1}$$

It follows that at pH 4.3 and $\Sigma m_{Ge} > 0.005m$ the concentration of the poly-ions $\{[Ge(OH)_4]_8(OH)_3\}^{3-}$ is eight orders of magnitude lower than the concentration of the monomers, that is, the concentration of the charged polynuclear species is negligibly small.

The maximal Ge concentration in the solution when all the germanium is in the form of uncharged monomeric species corresponds to curve 2 (2′) in Fig.1. The experimental curve 1 lies above curve 2 (2′), that is, the solution also contains (besides monomeric species) uncharged polymeric species of germanium. The reduction in the solubility of $GeO_{2\,hex}$ to its minimal value in both acidic and alkaline ranges shows the decomposition of the uncharged polynuclear species to the neutral species $Ge(OH)_4^0$.

Equilibrium in the GeO_2-H_2O System at 25 °C (Monomeric Forms).

The formation of germanium-containing monomeric species in the presence of $(OH)^-$ anions, can be written as follows:§

$$GeO_2+2H_2O=Ge(OH)_4{}^0, \tag{2}$$

$$Ge(OH)_4{}^0+(OH)^-=GeO(OH)_3{}^-+H_2O, \tag{3}$$

$$GeO(OH)_3{}^-+(OH)^-=GeO_2(OH)_2{}^{2-}+H_2O. \tag{4}$$

The equilibrium constants of reaction (3) have been determined by various investigators $\lg K_3 = 4.415$;[18] 5.505;[18] 5.69;[24] 5.116;[25] 4.898;[22] and 4.65.[13] The most reliable values were given by Ingri[13] who allowed for the formation of polynuclear anions.

Ingri[13] determined the concentration equilibrium constants of reaction (3) at an ionic strength of 0.5 ($\lg K = 4.65 \pm 0.5$); on assuming $\gamma_{(OH)^-} = \gamma_{GeO(OH)_3^-}$, as the singly-charged ions the thermodynamical equilibrium constant of reaction (3) can be regarded as equal to the concentration ones.

The thermodynamic formation constant of the doubly-charged anion $GeO_2(OH)_2^{2-}$ was calculated by the Vasil'ev equation:[26]

$$\lg K_c - \frac{\Delta Z^2 S_T\sqrt{I}}{1+1.6\sqrt{I}} = \lg K^0 + b$$

where ΔZ^2 is the algebraic sum of the squares of the charges of the ions participating in the reaction, I the ionic strength of the solution, K_c the concentration, and K^0 the thermodynamic solubility constant. The quantities S_T were taken from a handbook,[27] the concentration constants of reaction (4) (at $I = 0.5$, $\lg K_4 = 1.46 \pm 0.13$; at $I = 3$, $\lg K_4 = 1.64 \pm 0.03$) were taken from published papers.[13,21] The value obtained for $\lg K_4^0$ was 1.23 ± 0.25.

Consistent results on the behaviour of quadrivalant germanium in acid solutions have not been obtained. Pugh[16] concluded on the basis of experiments with cation-exchange resins that in the pH range 7–1 cationic species of germanium do not exist in the solution. Other work,[28–30] however, suggested the existence of germanium cations even in weakly acidic solutions. Spectrophotometric data from these studies were used to derive the hydrolysis constants for the following mononuclear cations of germanium at 25 °C and ionic strengths of 0.1, 0.3, 0.5, 1.0, and 8.8:

$$Ge^{4+}+H_2O=Ge(OH)^{3+}+H^+, \tag{5}$$

$$Ge(OH)^{3+}+H_2O=Ge(OH)_2{}^{2+}+H^+, \tag{6}$$

$$Ge(OH)_2{}^{2+}+H_2O=Ge(OH)_3{}^++H^+, \tag{7}$$

$$Ge(OH)_3{}^++H_2O=Ge(OH)_4{}^0+H^+. \tag{8}$$

By extrapolation to zero ionic strength at 25 °C, values were obtained[28–30] of $\lg K_5^0 = 0.11$; $\lg K_6^0 = -0.26$; $\lg K_7^0 = -0.52$; and $\lg K_8^0 = -0.72$. The constants used in the calculation had been obtained in more precise form—according to the Vasil'ev equation:[31] $\lg K_5^0 = -0.78$; $\lg K_6^0 = -0.16$; $\lg K_7^0 = -0.36$; and $\lg K_8^0 = -0.88$.

The results given above on the equilibrium constants for the hydrolysis of Ge^{4+}, $Ge(OH)^{3+}$, $Ge(OH)_2^{2+}$ and $Ge(OH)_3^+$, and on the equilibrium constants for the formation of the hydroxo-complexes $GeO(OH)_3^-$, and $GeO_2(OH)_2^{2-}$ were used to calculate the theoretical solubility curve assuming the solution in equilibrium with $GeO_{2\,hex}$ to involve a predominance of cationic (Fig.1, curve 4) or of anionic (curve 3) hydroxo-complexes. The calculated curves 3 and 4 do not coincide with the experimental solubility curve of GeO_2. At pH > 9 curve 1 corresponds to the solubility of the polygermanates, and not that of $GeO_{2\,hex}$, and curve 3, constructed on the basis of the equilibrium constants for the formation of the hydroxo-complexes $GeO(OH)_3^-$ and $GeO_2(OH)_2^{2-}$ must be assigned to the metastable equilibrium in the GeO_2-H_2O system. According to Nazarenko and Flyantkova,[30] if germanium in the acid region is present as the cations Ge^{4+}, $Ge(OH)^{3+}$, $Ge(OH)_2^{2+}$, and $Ge(OH)_3^+$, then the solubility at pH < 1 should be changed in accordance with curve 4. However, the form of the experimental curve for the solubility of $GeO_{2\,hex}$ in this pH range shows that Pugh's results[16] which indicate the absence of cationic species of GeO_2 in the solution are more reliable, and hence the hydrolysis [reactions (5)–(8)] does not occur.

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§Depending upon the coordination number of the germanium in the solution, which by analogy with the solid phase can be equal to 4 or 6, the composition of the Ge-containing species can be written with various numbers of water molecules—for example, $Ge(OH)_4.2H_2O$ or $GeO(OH)_3^-.2H_2O$. In subsequent thermodynamic calculations the formulae given above for the hydroxo-complexes are used, since the change in free energy of hydration in the stationary state equals zero.

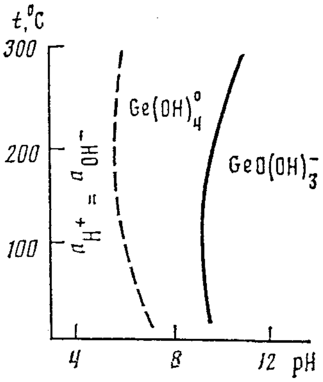

Figure 2. Relation between the germanium hydroxo-complexes in neutral and alkaline regions as a function of temperature, calculated according to Eqn.(10).

Hence it can be assumed that, as for silicon (the SiO_2-H_2O system), cationic species are absent from the GeO_2-H_2O system. The germanium system differs from the SiO_2-H_2O system, where at pH 1–9 the silicon is present as the species $Si(OH)_4^0$,[32] in that neutral species of germanium in the solution can include not only mononuclear but also polynuclear varieties. The presence of germanium polynuclear species in the solution rationalises the observation that the solubility of $GeO_{2\,hex}$ (as a metastable phase) is three orders of magnitude greater than that of quartz.

Behaviour of GeO_2 at Elevated Temperatures

The temperature dependence of the equilibrium constant of reaction (3) was determined up to 300 °C. $\Delta S^0_{298.15}$ and ΔC_p for reaction (3) are numerically equal to the corresponding quantities for the reaction

$$Si(OH)^0_{4\,soln.} + (OH)^-_{soln.} = SiO(OH)^-_{3\,soln.} \tag{9}$$

given by Sorokin and Dadze.[33] Then

$$\lg K_{T^0} = \frac{3312.21}{T} - 7.7184 + 0.004\,32\ T \tag{10}$$

The thermodynamic data necessary for estimating the temperature dependence of the constants of reaction (4) are not available.

The temperature dependence of the equilibrium constants of reaction (3) which we calculated allowed us to find the relationship between the germanium hydroxo-complexes $Ge(OH)_4^0$ and $GeO\cdot(OH)_3^-$ at various temperatures and as a function of the pH of the solution (Fig.2): the fields of predominance of the germanium hydroxo-complexes is weakly dependent on the temperature. To estimate the temperature dependence of the corresponding equilibrium constants of reactions (5)–(8) using, as for reactions (3)–(4) the analogy with the silicon-containing system, is impossible: in the acid range in the SiO_2-H_2O system there are no cationic silicon species, and the $Si(OH)_4^0$ molecules predominate even in extremely concentrated solutions of such strong acids as HCl and HNO_3, over a wide temperature range (25–400 °C).[33]

Solubility of GeO_2 in Water at Elevated Temperatures

To determine the experimental solubility equilibrium of $GeO_{2\,hex}$ at temperatures exceeding 100 °C was impossible, since under these conditions the change $GeO_{2\,hex} \rightarrow GeO_{2\,tetr}$ is observed; the amount of the latter in the solid phase increases with the duration of the experiment.[34] In the range 25–100 °C, the solubility of $GeO_{2\,hex}$ is described by the equation:

$$\lg m_{GeO_2} = -\frac{767}{T} + 1.207\,. \tag{11}$$

The solubility of $GeO_{2\,tetr}$ was studied earlier[34–36] in the temperature range 25–300 °C, at pressures from s.v.p. to 140 MPa (Fig.3). The solubility of the rutile modification of GeO_2 in this temperature interval is described by the equation:

$$\lg m_{Ge(OH)_4^0} = -\frac{4132}{T} + 11.969 - 0.011\,56\ T \tag{12}$$

and in the temperature interval 100–300 °C by the linear equation:

$$\lg m_{Ge(OH)_4^0} = -\frac{1774}{T} + 1.403\,. \tag{13}$$

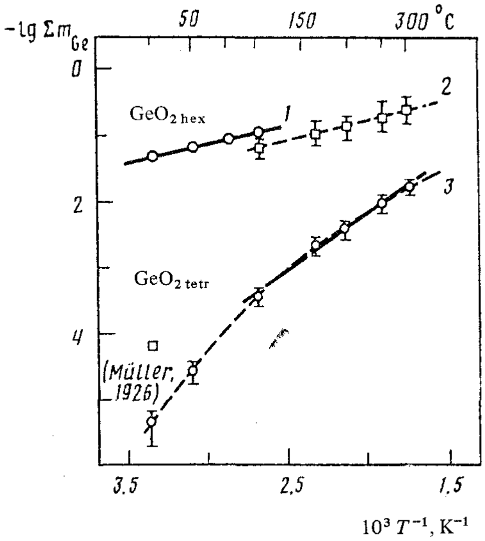

Figure 3. Solubility of germanium dioxide in water in the temperature range 25–300 °C. (1) Solubility of $GeO_{2\,hex}$, calculated from published results; (2) solubility of $GeO_{2\,hex}$, calculated from data on the solubility of $GeO_{2\,tetr}$ and Eqn.(16); (3) solubility of $GeO_{2\,tetr}$ (experimental results).

The effect of pressure in the temperature interval investigated on the solubility of $GeO_{2\,tetr}$ was minimal. On raising the temperature from 100° to 300 °C the solubility of $GeO_{2\,tetr}$ rises from 3.8×10^{-4} to 1.7×10^{-2} *m*. These values are significantly lower than the solubility of metastable $GeO_{2\,hex}$.

The independence of the solubility of $GeO_{2\,tetr}$ and the pH (2–9) at constant temperature, the low absolute values of the solubility at 100–300 °C, and the influence of temperature, which facilitates the occurrence of depolymerisation, all show that under high-temperature conditions germanium dissolves in the solution predominantly in the form of uncharged species (Fig.2):

$$GeO_{2\,tetr} + 2H_2O_L = Ge(OH)^0_{4\,soln}. \qquad (14)$$

The solubility curves for the two modifications of GeO_2 intersect at the point for the phase transformation, at 1308 K, $\Delta G_{1308} = 0$. The changes in Gibbs free energy ΔG°_T for the transformation

$$GeO_{2\,tetr} \rightleftarrows GeO_{2\,hex} \qquad (15)$$

in the interval 25 – 300 °C are calculated from the thermodynamic data, independent of the solubility data. The equations for the temperature dependence of the heat capacity for $GeO_{2\,tetr}$ and $GeO_{2\,hex}$ in the ranges 298.15 – 1308 and 298.15 – 1388 K are respectively:[37]

$$C_p = 78.195 - 10.079 \times 10^{-3}T - 22.974 \times 10^5 T^{-2} + 9.230 \times 10^{-6}T^2,$$

$$C_p = 62.208 + 14.230 \times 10^{-3}T - 12.765 \times 10^5 T^{-2}.$$

Hence for reaction (15):

$$\Delta C_p = -15.987 + 24.309 \cdot 10^{-3}T + 10.209 \cdot 10^5 T^{-2} - 9.230 \cdot 10^{-6} T^2. \qquad (16)$$

Using published data[38,39] for reaction (15); then $\Delta H^\circ_{966} = 21.5 \pm 1.3$ kJ mole^{-1}. This value corresponds to $\Delta H_{298.15} = 22.3 \pm 1.7$ and $\Delta H_{1308} = 21.7 \pm 1.7$ kJ mole^{-1}.

Since $\Delta G^\circ_{1308} = 0$ at the phase transformation temperature then $\Delta S^\circ_{1308} = \Delta H^\circ_{1308}/1308 = 16.6 \pm 1.3$ JK^{-1} mole^{-1}. This value corresponds to $\Delta S_{298.15} = 17.7 \pm 1.5$ JK^{-1} mole^{-1}. Hence for reaction (15):

$$\Delta G_T{}^0 = 29\,492 - 123{,}71\ T + 15{,}99\ T \ln T - 12{,}15 \cdot 10^{-3}\ T^2 - 5{,}10 \cdot 10^5\ T^{-1} + 1{,}54 \cdot 10^{-6}\, T^3.$$

From a knowledge of ΔG°_T it is possible to calculate the value of $\lg K^\circ_T$ for equation (15) since $\Delta G^\circ_T = -RT \ln K^\circ$ (Table 1).

Table 1.

t, °C	T, K	$\lg K_{14}$	$\lg K_{15}$	$\lg K_{17}$
25	298.15	−4.23	−2.98	−1.25
100	373.15	−3.35	−2.20	−1.15
160	433.15	−2.69	−1.76	−0.93
190	463.15	−2.43	−1.56	−0.84
250	523.15	−1.99	−1.30	−0.69
300	573.15	−1.69	−1.11	−0.58

The thermodynamic equilibrium constant of reaction (14) can be taken as equal to the concentration of $Ge(OH)^0_4$;

$$\lg K_{14}{}^0 = \lg m_{Ge(OH)_4{}^0},$$

since the activities of $GeO_{2\,tetr}$ and H_2O in the standard state equal unity and the activity coefficient of $Ge(OH)^0_4$ as an uncharged species at a moderate concentration can be taken as equl to unity. Assuming an identical dissolution mechanism for $GeO_{2\,tetr}$ and $GeO_{2\,hex}$, the reaction for the dissoultion of $GeO_{2\,hex}$ can be written in the form

$$GeO_{2\,hex} + 2H_2O_L = Ge(OH)^0_{4\,soln}. \qquad (17)$$

Then the equilibrium constant of reactino (17) can be calculated from the difference ($\lg K_{14} - \lg K_{15}$) (Table 1). Assuming that

$$\lg K_{17} = \lg m_{Ge(OH)_4{}^0},$$

we can determine the concentration $Ge(OH)^0_4$ in equilibrium with $GeO_{2\,hex}$. The solubility curve thus obtained (Fig.3) lies below the experimental curve for $GeO_{2\,hex}$, which agrees with the hypothesis the solution in equilibrium with $GeO_{2\,hex}$ also contains polynuclear species.

On the basis of the thermodynamic properties for $GeO_{2\,tetr}$[37] and the results of our experiments we calculated the thermodynamic properties of the hydroxo-complexes $Ge(OH)^0_4$ and $GeO(OH)^-_3$ in aqueous solution in the temperature range 25 – 300 °C. The magnitude of the free energies of formation of the hydroxo-complexes of germanium can be calculated from the equilibrium constants for the dissolution of germanium dioxide $GeO_{2\,tetr}$ [reaction (14)], and for the formation of the monomeric singly-charged ion $GeO(OH)^-_3$ [reaction (3)], according to Eqn.(10). The thermodynamic properties of H_2O_L and $(OH)^-_{soln}$ were taken from a handbook,[27] and the values of $\Delta G_{fT}GeO_{2\,tetr}$ from Ref.37.

Table 2 gives the free energy of formation of the hydroxo-complexes $Ge(OH)^0_4$ and $GeO(OH)^-_3$.

Table 2.

t, °C	T, K	$\Delta G^0_{f,T}$ GeO_{2tetr}	$\Delta G^0_{f,T}$ $H_2O_{liq.}$	ΔG_{OH^-}	$\Delta G_{f,T}$ $Ge(OH)_4{}^0$	$\Delta G_{f,T}$ $GeO(OH)_3{}^-$
25	298.15	−521.64	−56.687	−37.594	−609.06	−563.25
50	323.15	−516.73	−55.726	−36.12	−602.90	−559.00
100	373.15	−506.91	−53.834	−32.92	−590.64	−549.94
150	423.15	−497.12	−51.994	−29.40	−578.51	−540.22
200	473.15	−487.38	−50.198	−25.58	−566.52	−529.84
250	523.15	−477.68	−48.436	−21.38	−554.64	−518.84
300	573.15	−468.03	−46.69	−16.82	−542.84	−507.08

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Solubility in the Lithium Nitrate-Calcium Nitrate-Acetone and Lithium Nitrate-Calcium Nitrate-Propan-2-ol Systems

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Solubility at 298.15 K has been studied in the $LiNO_3$-$Ca(NO_3)_2$-L systems, where L is propan-2-ol or acetone, by isothermal saturation and also by measurement of the density and the refractive index of saturated solutions. *The systems are simple eutonic.*

The work now described is a continuation of studies of the influence of macrophysical properties and structural features of non-aqueous solvents on the formation of solid phases in systems containing lithium and calcium nitrates.

The $LiNO_3$ and $Ca(NO_3)_2$ used were purified by the method described earlier.[1] "Special purity" grade acetone was purified and dried with molecular sieves, and "chemically pure" grade propan-2-ol was dried as described in a handbook.[2] The amount of water remaining in the acetone was checked on a Tsvet-100 chromatograph; that in the propan-2-ol by the Karl Fischer method. The water in the solvents was: 0.02 + 0.01% in the acetone, 0.01 ± 0.01% in the propan-2-ol. The experimental method and the analytical determination of the phase equilibria were as described earlier.[1]

Solubility and solid phases in the lithium nitrate—calcium nitrate—acetone and lithium nitrate—calcium nitrate—propan-2-ol systems.

Composition of liquid phase			Composition of solid phase, mass %		Solid phase
mass % $Ca(NO_3)_2$	mass % $LiNO_3$	mole fraction $Ca(NO_3)_2$	$Ca(NO_3)_2$	$LiNO_3$	
The lithium nitrate-calcium nitrate-acetone system					
–	5.61	–	–	–	$LiNO_3$
2.42	6.72	0.0087	0.36	92.44	ditto
3.48	7.87	0.013	0.90	76.97	»
6.30	8.69	0.023	1.20	87.30	»
10.98	11.46	0.042	1.12	91.29	»
14.23	11.73	0.055	3.96	78.76	»
15.52	11.68	0.061	2.63	86.01	»
18.23	12.38	0.073	1.85	93.07	»
23.53	12.52	0.098	7.24	74.23	»
27.02	13.72	0.12	4.35	85.46	»
30.60	12.17	0.14	7.10	82.39	»
33.49	12.41	0.15	7.52	82.38	»
37.04	9.83	0.17	43.06	20.17	$LiNO_3$, $Ca(NO_3)_2$
26.30	8.77	0.11	83.21	2.62	$Ca(NO_3)_2$
19.45	7.89	0.079	90.12	1.05	ditto
18.67	8.60	0.075	62.12	3.94	»
18.54	6.41	0.075	53.29	4.06	»
16.28	5.25	0.064	66.99	3.62	»
12.78	3.89	0.049	55.67	2.37	»
12.03	3.41	0.046	84.24	0.86	»
9.71	2.59	0.037	56.21	1.62	»
3.90	–	0.014	–	–	»
The lithium nitrate-calcium nitrate propan-2-ol system					
–	14.66	–	–	–	$LiNO_3$
1.37	14.70	0.0051	0.23	94.91	ditto
8.31	14.06	0.032	1.63	85.00	»
10.94	13.87	0.045	2.68	85.37	»
16.17	12.94	0.066	3.33	82.80	»
18.49	12.19	0.077	42.24	38.79	$LiNO_3$, $Ca(NO_3)_2$
13.05	10.08	0.052	69.69	3.72	$Ca(NO_3)_2$
11.92	7.38	0.047	74.00	2.56	ditto
10.12	5.81	0.040	78.49	1.38	»
8.39	5.29	0.032	85.97	0.93	»
6.44	3.54	0.025	90.51	0.48	»
4.61	3.01	0.017	83.77	0.64	»
4.01	0.88	0.015	85.94	0.94	»
3.28	–	0.12	–	–	»