

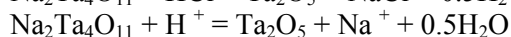
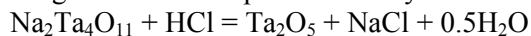
EXPERIMENTAL EVIDENCE FOR THE TEMPERATURE MAXIMUM OF NaCl HYDROLYSIS REACTION AT HIGH T-P CONDITIONS

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The hydrolysis reaction of NaCl at fixed Na₂O activity defined by buffer Na₂Ta₄O₁₁ -Ta₂O₅ assemblage, was investigated experimentally at 100-700°C, 1, 500-2000 bars and concentration NaCl from 0.1 up to 50m. The following reactions take place in this system:



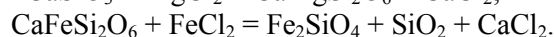
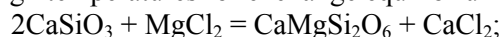
The assemblage Na₂Ta₄O₁₁ -Ta₂O₅ is advantageous over that of conventionally used albite-andalusite-quartz (AAQ), in that: a) the concentration of HCl in equilibrium with this assemblage is approximately one order of magnitude higher which allows to reliably measurements using pH-method; b) the solubility of Ta₂O₅ in the fluid is much lower than SiO₂ and Al₂O₃ and consequently, the influence of various quench effects is minimized; c) the phases Na₂Ta₄O₁₁ and Ta₂O₅ are stable in a wide range of T and P in contrast to albite, which has a variable degree of ordering, and Al₂SiO₅, which has three polymorph modifications.

The experiments were performed by autoclave-capsule method in static conditions. The concentration of HCl was measured by pH-method. At the concentration of NaCl over 1m the concentration of HCl was measured in the distillate after treatment of the quenched solutions.

High temperature area. As expected by analogy with result on AAQ assemblage the NaCl/HCl ratio increases with temperature decreasing up to 400°C. The S-shape changes of equilibrium HCl concentration with increasing NaCl concentration is observed on the 700 and 600°C isotherms at P 1 kbars. This is a consequence of immiscibility of the H₂O-NaCl system at high temperatures and low fluid density. The HCl values, that fall between the maximum and minimum of HCl concentration result from the mixing of liquid and gas phases on quenching. Within the pressure range from 500 to 1000 bars the NaCl/HCl ratio at T=700°C rises slightly with pressure. The hydration number of associated NaCl is approximately 1.2 at the fluid density < 0.3 g/cm³. Further increase of pressure up to 2000 bars results in sharp decrease of equilibrium HCl concentration due to increasing degree of NaCl° dissociation (fig. 1.).

Low temperature area. The unexpected results were obtained at low temperature in homogeneous area. The temperature dependence of hydrolysis reaction is changes to reverse and at T 300°C the equilibrium HCl concentration is higher, than at 400°C (Fig. 1). The position of this equilibrium at 200°C was defined with large error bars, due to the kinetic limitation of the reaction. The additional experiment was executed at T 100°C and saturated pressure, which has confirmed the existing of extreme in temperature dependence of NaCl/HCl ratio of given reaction.

It was found early [1,2] the similar temperature dependence in Ca/Mg and Ca/Fe ratios (like to hydrolysis reaction) is displayed at high temperatures for exchange equilibrium:



The experiments, with these exchange equilibria were carried out at 200°C and 2 kbars. The results have also revealed extreme relationships in the temperature dependence concentration ratios regarded to components in low temperature area (fig. 2 and 3).

The attempts to reproduce such extreme behavior of component ratios with the thermodynamic simulations (Shvarov program HCh version 3.2), taking as an example the hydrolysis reaction of the albite-andalusite-quartz assemblage were not successful (fig. 4).

The extreme behavior of NaCl hydrolysis reaction may be explained by sharp increase in HCl° degree of dissociation with decreasing of temperature. The absence of data on HCl° dissociation constant in pure water obtained by the electric conductivity method at low temperatures indicates that at low temperatures HCl is stronger electrolyte, than NaCl. According to the various data the values of K_{DHCl}, in particular at 25°C, vary from 0,6 up to 6 log. units [3]. By analogy the extreme changes Ca/Mg and Ca/Fe ratios with decreasing the temperature can be explained by higher degree of dissociation MgCl₂ and FeCl₂ relatively to CaCl₂ or by presence some others Mg and Fe species in solution.

The revealed extreme temperature behavior of hydrolysis reaction can explain the manifestation of late alkaline low-temperature stage at the temperature evolution of hydrothermal solution, distinguished by D.S.Korzhinskii [4].

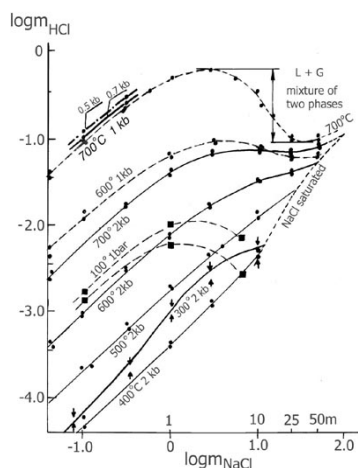


Fig. 1. The concentration of HCl in the fluid at fixed activity of Na_2O buffered by assemblage $\text{Ta}_2\text{O}_5 - \text{Na}_2\text{Ta}_4\text{O}_{11}$.

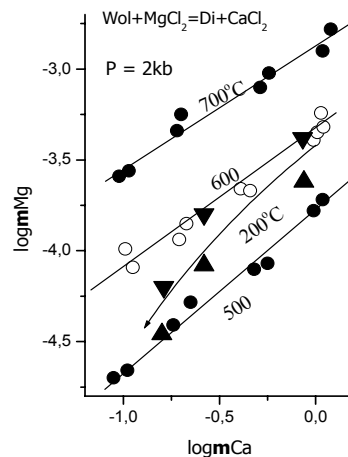


Fig. 3. The ratio of Ca/Mg in the fluid in equilibrium with diopside-wollastonite assemblage.

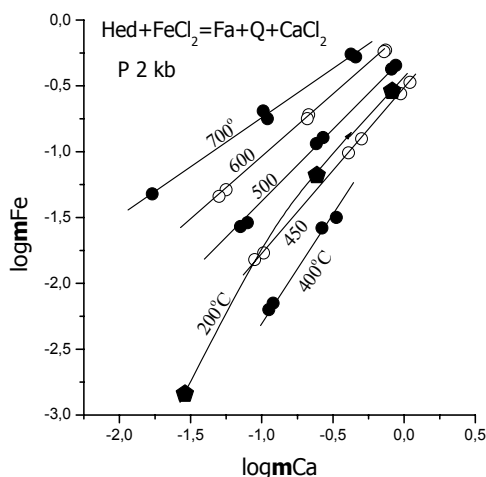


Fig. 2. The ratio of Ca/Fe in the fluid in equilibrium with hedenbergite-quartz-fayalite assemblage.

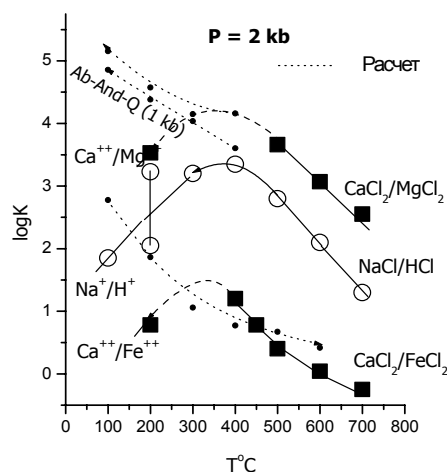


Fig. 4. The comparison of experimental and calculated (HCh Shvarov program, version 3.2) constants of considered equilibrium.

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