

SOLUBILITY OF CORUNDUM IN AQUEOUS ALKALINE
SOLUTIONS AT ELEVATED TEMPERATURES AND PRESSURES

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Dependence of the Solubility of Corundum on Pressure. Barns, Laudise, and Shields [1] have shown that the pressure dependence of the solubility of corundum ($\alpha\text{-Al}_2\text{O}_3$) in aqueous solutions of sodium carbonate is complex. For example, at 430°C , the solubility of corundum in 3.4 m Na_2CO_3 increases with an increase in pressure up to 1380 bars, but a further increase in pressure has no effect on the solubility, and even possibly decreases it somewhat. It is also known that the solubility of sodium carbonate in water at elevated temperatures depends greatly on pressure [2]. It might well be assumed that the solubility of corundum in aqueous solutions of sodium carbonate depends directly on the state of the Na_2CO_3 in the system.

The results of an experimental confirmation* of this assumption are shown in Fig. 1.

A comparison of the experimentally determined pressure dependence of the solubility of corundum in aqueous Na_2CO_3 at 460° with the pressure dependence of the solubility of Na_2CO_3 in water at this same temperature [2] indicates that the increase in corundum solubility with increasing pressure (at constant solution concentration) continues until all of the Na_2CO_3 introduced into the system has gone into solution. A further increase in pressure has a very slight effect on the solubility of corundum.

*The solubility of corundum was studied in 50-ml autoclaves equipped with tightly fitting protective silver inserts by determining the loss in weight following quenching [1, 3]. Synthetic corundum leaves and cp reagents were used in the experiments. According to Kuznetsov [3], solution of corundum under hydrothermal conditions requires 1.5 days for establishment of equilibrium. On this basis, we elected to hold our solutions at the given temperature and pressure for from 2 to 5 days, since this ensured that equilibrium was reached in the system. The pressure under any set of experimental conditions was determined from the P-F-T diagrams published by Samoilovich for aqueous solutions of sodium carbonate and sodium hydroxide [4]. The temperature was held at the desired value within $\pm 3^\circ$.

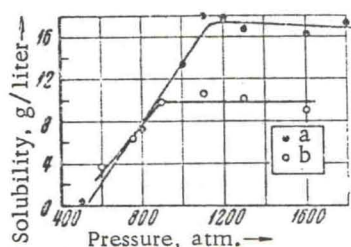


Fig. 1

Fig. 1. Dependence of the solubility of corundum in aqueous sodium carbonate solutions on pressure at 460° . Na_2CO_3 concentration: a) 50 g/liter; b) 25 g/liter.

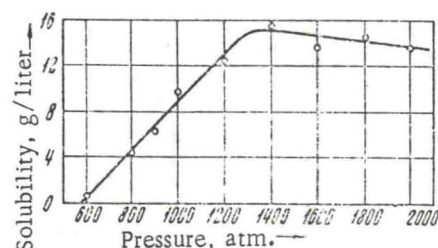


Fig. 2

Fig. 2. Pressure dependence of the solubility of corundum in aqueous NaHCO_3 with a concentration of 100 g/liter at 500° .

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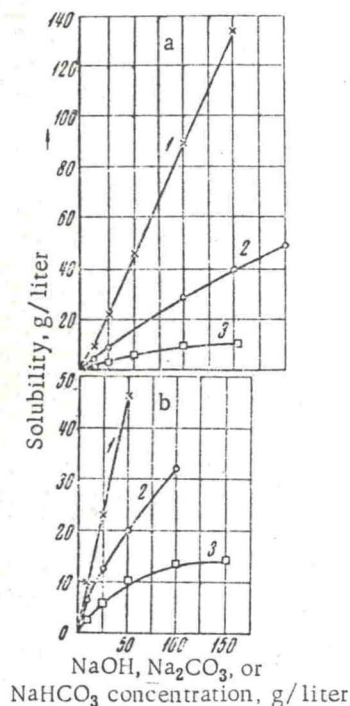


Fig. 3. Dependence of the solubility of corundum in aqueous solutions of NaOH (1), Na₂CO₃ (2), and NaHCO₃ (3) on concentration at temperatures of 460 (a) and 500° (b) (1600 atm pressure).

Our experimental results are shown in Fig. 3. It is evident from the figure that the curves relating corundum solubility to electrolyte concentration differ.

The dependence of corundum solubility in aqueous NaOH on the concentration of base is linear over the entire range of concentrations studied. According to the data of Barns et al. [1], the linear dependence of corundum solubility on NaOH concentration holds up to the highest concentration studied, 10 m.

A similar constancy of the corresponding ratios of dissolved substance to solvent was not observed for aqueous solutions of Na₂CO₃ and NaHCO₃. An analogous phenomenon, ascribed to hydrolysis of the salt, has been observed with aqueous solutions of Na₂B₄O₇ and K₂CO₃ [5].

On the basis of the above material, it may be concluded that solution of corundum in aqueous solutions of hydrolyzable salts (Na₂CO₃, K₂CO₃, NaHCO₃, Na₂B₄O₇) at elevated pressures and temperatures is determined wholly by the amount of alkali metal hydroxide dissolved as a result of hydrolysis.

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LITERATURE CITED

1. R. L. Barns, R. A. Laudise, and R. M. Shields, *J. Phys. Chem.*, **67**, 4, 835 (1963).
2. M. I. Ravich and F. E. Borovaya, *Dokl. Akad. Nauk SSSR*, **156**, No. 4, 894 (1964); **180**, No. 6, 1372 (1968).
3. V. A. Kuznetsov, Investigation of the Crystallization of Corundum Under Hydrothermal Conditions. Dissertation. Institute of Crystallography, Academy of Sciences of the USSR, Moscow 1967.
4. L. A. Samoilovich, Experimental Investigation of Thermodynamic Relationships of Mineral-Forming Solutions (as Applied to Thermobarometry and the Growth of Crystals). Dissertation, Moscow State University 1968.
5. S. Levinson, G. Douglas, and L. R. Johnson, *Am. Mineral.*, **50**, 3/4, 403 (1965).

It should be mentioned that the solubility of sodium carbonate in water increases in the presence of aluminum oxide [3]. This is because part of the sodium carbonate takes part in the dissolution of the aluminum oxide through the formation of aluminate complexes. A comparison of data on the solubility of corundum in aqueous Na₂CO₃ (our data and those of Barns et al. [1]) with data on the solubility of Na₂CO₃ in water makes possible an approximate estimate of the increase in solubility of Na₂CO₃ in the presence of aluminum oxide. The time at which all of the sodium carbonate was dissolved was taken to be that at which a further increase in pressure caused no further increase in the solubility of corundum (the inflection points on the curves showing the dependence of corundum solubility on pressure at constant temperature and solution concentration). It was not difficult to determine from the data of Ravich and Borovaya [2] the solubility of Na₂CO₃ in water at the same temperature and at the pressure corresponding to the inflection point. This analysis revealed that the solubility of Na₂CO₃ increases by ~20-25% in the presence of aluminum oxide.

The experimental results of the study of the solubility of corundum in aqueous NaHCO₃ as a function of pressure are shown in Fig. 2.

As in the case of the Na₂CO₃ solutions, with an increase in pressure the solubility of corundum in the NaHCO₃ solution at first increased (up to ~1400 atm), and then decreased somewhat. On the basis of these results, it would be expected that the solubility of NaHCO₃ in water, like the solubility of Na₂CO₃, would depend greatly on pressure.

Dependence of the Solubility of Corundum on Solution Concentration. In order to avoid the possible presence of undissolved sodium carbonate or bicarbonate in the system, which would alter the results of experiments at high concentrations of Na₂CO₃ or NaHCO₃, all studies of the dependence of corundum solubility on concentration were carried out at a pressure of ~1600 atm. The solubility of corundum in NaOH solutions does not depend on pressure [1].