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SOLUBILITY OF SODIUM CARBONATE IN WATER AT ELEVATED TEMPERATURES AND PRESSURES

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This article gives the results of determinations of the solubility of sodium carbonate in water in the temperature interval 200–500° at various pressures, reaching 1500–2400 kg/cm^2.

The solubility of anhydrous sodium carbonate in water in the presence of a vapor phase (i.e., at pressures equal to the vapor pressures of the solutions) is characterized by a negative temperature coefficient and, at temperatures approaching the critical temperature of water, becomes very small (^{1}). Judging by the rapid decrease in the solubility of anhydrous sodium carbonate with increasing temperature, the parameters corresponding to the first critical point of the system Na_2CO_3—H_2O are close to the critical parameters of pure water. Therefore the results of determinations of the solubility of sodium carbonate at 400, 450, and 500°, i.e., at temperatures exceeding the critical temperature of water, should be assigned to the solubility of this salt in the fluid phase.

Table 1

Solubility of sodium carbonate in water at elevated temperatures and pressures

P, kg/cm^2	Na_2CO_3, wt. %	P, kg/cm^2	Na_2CO_3, wt. %	P, kg/cm^2	Na_2CO_3, wt. %
200 °C		**400 °C**		**500 °C**	
1130	28	400	~1	900	~1
2370	30.5—31	500	1.8	1200	2.5
300 °C		700	4—4.5	1505	7.5
295	13	903	8—8.5		
600	19.5	1050	13—13.5		
900	23	1125*	15		
1200	26.5—27	1205	18.5		
1400	27.5	1320	21—21.5		
1985	29.5	1350*	22.5		
2385	31	1400	26.5		

P, kg/cm^2	Na$_2$CO$_3$, wt. %	P, kg/cm^2	Na$_2$CO$_3$, wt. %	P, kg/cm^2	Na$_2$CO$_3$, wt. %
350 °C		1460*	27.5		
200	2.7	2065	38		
500	7.5—8	**450 °C**			
600	9.5	700	~1		
800	14.5	903	2.5		
825*	15	1200	7—7.5		
903	16.5—17	1250*	10		
1185	24	1400	14		
1190*	24	1410*	15		
1412	27.5	1490*	22		
1555	29—29.5	1500	22		
1900	34	1580*	29		
		1670*	35		
		1750	37.5		
		1875	41.5		

* Obtained by the method of *P*—*V* curves.

To determine the solubility of sodium carbonate under the above parameters, the method proposed by us (as also in the earlier determinations of the solubility of sodium sulfate (2,3) and lithium sulfate (4)) was used (2,3). This method is based on obtaining, at constant temperature, the dependence of the pressure established in the autoclave after dissolution of the crystalline salt on the concentration of the solution charged or formed. Some of the curves obtained are shown in Fig. 1. These curves consist of two branches, corresponding to unsaturated and saturated (horizontal straight line) solutions; the point of intersection of these two branches directly indicates the concentration of the saturated solution of sodium carbonate at the corresponding parameters.

To confirm the results obtained, the method of *P*—*V* curves was also used, based on establishing (at constant temperature) the relationship between the pressure and the amount of mercury released from the autoclave (i.e., a quantity proportional to the increase in the volume of the system (2,3)). Some of the obtained *P*—*V* curves are shown in Fig. 2. These

the curves also consist of two branches, the point of intersection of which indicates the pressure at which crystallization of the charged sodium carbonate solution begins.

The results obtained in determining the solubility of sodium carbonate in water are given in Table 1 and shown in Fig. 3 in the form of isotherms expressing the dependence of the solubility of this salt on pressure at temperatures of 200, 300, 350, 400, 450, and 500°. The results obtained by means of both experimental methods are in good agreement with one another*.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Fig. 1. Experimental curves of the dependence of the pressure obtained after dissolution of crystalline sodium carbonate on the concentration of the charged or resulting solution. The numbers by the curves are the temperature in °C.

Fig. 2. *P*—*V* curves. To avoid superposition of the curves on one another, the origin of the abscissa coordinates has been shifted for each curve.

The initial points of the 200, 300, and 350° isotherms represent the solubility (without excess pressure) and the vapor pressure of saturated sodium carbonate solutions (6) at the corresponding temperatures.

The solubility of sodium carbonate without excess pressure at temperatures approaching the critical temperature of water becomes very small, but with increasing pressure it rises rapidly. At temperatures above the critical temperature of water, the solubility of sodium carbonate at relatively low pressures is negligible, but with a sufficient increase in pressure it also becomes very considerable.

The same substantial increase in salt solubility with increasing pressure at high temperatures was previously found by us in the systems sodium sulfate—water (2,3) and lithium sulfate—water (4).

In the sodium carbonate—water system, at relatively low temperatures (200 and 300°) the solubility isotherms are convex toward the composition axis, but already at 350° a convexity toward the pressure axis appears, which at higher temperatures (at 400 and especially at 450°) becomes more sharply expressed,

* Some results of determinations of the solubility of soda in water at high temperatures and pressures are available in the work (5).

However, at sufficiently high pressures, on the 350-450° isotherms a convexity toward the composition axis appears, which leads to the appearance of an inflection point on these isotherms. The course of the middle portions of these isotherms, with increasing temperature, approaches the horizontal.

In the temperature interval 200-450°, at pressures of about 1500 kg/cm^2, a change in the sign of the temperature coefficient of solubility of sodium carbonate occurs (intersection of the isotherms in Fig. 3). At relatively low pressures the solubility of this salt decreases with increasing temperature, whereas at pressures above 1500-1600 kg/cm^2 it increases.

Fig. 3. Isotherms expressing the dependence of the solubility of sodium carbonate in water on pressure: —determined by the *P*-*V* curve method, —solubility in the presence of a vapor phase. The numbers by the curves are the temperature in °C.

Fig. 3. Isotherms expressing the dependence of the solubility of sodium carbonate in water on pressure: —determined by the P-V curve method, —solubility in the presence of a vapor phase. The numbers by the curves are the temperature in °C.

Figure 2: Fig. 3. Isotherms expressing the dependence of the solubility of sodium carbonate in water on pressure: —determined by the P-V curve method, —solubility in the presence of a vapor phase. The numbers by the curves are the temperature in °C.

The noted features of the solubility of sodium carbonate in the fluid and liquid phases (the appearance of an inflection point on the solubility isotherms, the tendency of the middle portions of the isotherms, with increasing temperature, to approach the horizontal more and more, and the change in sign of the temperature coefficient of solubility) are also characteristic of the previously studied aqueous salt systems: sodium sulfate—water ([2],[3]) and lithium sulfate—water ([4]). These features are due, as was indicated in the corresponding papers, to the proximity of the three-phase region, which is apparently the upper three-phase region with the critical point Q (the second critical point of the system).

Apparently, in the sodium carbonate—water system these features are likewise due to the proximity of the upper three-phase region.

As a result of studying the solubility of sodium carbonate in water in the temperature interval 200-500° and at various pressures reaching 1500-2400 kg/cm^2, it has been found:

Within the limits of the parameters investigated, the solubility of sodium carbonate in water at constant temperature increases with increasing pressure, this increase being especially considerable at temperatures exceeding the critical temperature of water.

At pressures below 1500-1600 kg/cm^2 the temperature coefficient of solubility of sodium carbonate is negative, whereas at higher pressures it is positive. With increasing temperature, the form of the solubility isotherms changes regularly: an inflection point appears, and the course of the middle portion of the isotherms approaches the horizontal. The noted features, as in the previously studied systems sodium sulfate—water and lithium sulfate—water, are explained by the proximity of the upper three-phase region.

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