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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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SOLUBILITY OF LITHIUM SULFATE IN WATER AT ELEVATED TEMPERATURES AND PRESSURES

(Presented by Academician I. I. Chernyaev, December 27, 1963)

The solubility of lithium sulfate in water at elevated temperatures and at pressures equal to the vapor pressure of the saturated solutions (i.e., in the absence of a vapor phase) was determined previously (1, 2). At temperatures below 233°

Fig. 1. Experimental curves for the dependence of the pressure obtained after dissolution of crystalline lithium sulfate on the concentration of the loaded (a) or formed (b) solution. The numbers beside the curves are the temperature in °C.

in equilibrium with the saturated liquid solution there exists lithium sulfate monohydrate (1, 3, 4); above 233°—the anhydrous salt, whose solubility decreases with increasing temperature (1).

The present article gives the results of determinations of the solubility of lithium sulfate in water in the temperature interval 248-388° at various pressures reaching up to ~1000 kg/cm^2.

Determinations of the solubility of lithium sulfate at temperatures below the critical temperature of water (248-373°) were carried out at pressures exceeding the vapor pressure of saturated solutions of this salt, i.e., in the absence of a vapor phase (two-phase region: solid salt + saturated liquid solution).

Judging from the rapid decrease in the solubility of anhydrous lithium sulfate with increasing temperature, the parameters corresponding to the first critical point of the system Li_2SO_4—H_2O are close to the critical parameters of pure water. Therefore, the results of determinations of the solubility of lithium sulfate at 388°, i.e., at a temperature slightly exceeding the critical temperature of water, may be assigned to the solubility of this salt in the fluid phase.

Table 1

Solubility of lithium sulfate in water at elevated temperatures and

pressures

P, kg/cm^2	Li_2SO_4, wt. %	P, kg/cm^2	Li_2SO_4, wt. %
248°		**373°***	
347	26	500	4
642	28.5	700	14
925	30.5	858	30
		995	37
298°		**388°***	
293	19	600	3
570	25.5	790	13.5
890	30	838	24.5
		890	37.5
		1005	42.5
348°			
400	6.3		
600	16.5		
795	28		
948	33.5		
1070	36		

* At 373° and a pressure of 300 kg/cm^2, and likewise at 388° and a pressure of 400 kg/cm^2, as a result of the dissolution of the salt in pure water, the pressure dropped only slightly. Comparison of this pressure drop with the pressure drop in other determinations shows that, at the indicated parameters, the solubility of Li_2SO_4 is less than 1 wt. %.

Determinations of the solubility of lithium sulfate in water at elevated pressures were carried out using the apparatus (mercury autoclave) and experimental procedure proposed and described by us earlier ([5], [6]). This procedure is based on the fact that, when a crystalline salt dissolves in its unsaturated solution (at specified parameters), the system contracts, as a result of which the pressure inside the autoclave decreases. From the results of determinations (at a specified temperature and initial pressure) of the pressure values obtained after dissolution of the salt, a curve is constructed expressing the dependence of this pressure on the concentration of the loaded or resulting solution.

These curves consist of two branches, corresponding to unsaturated and saturated solutions; the point of intersection of these two branches indicates the desired concentration of the solution saturated at the corresponding parameters.

Some of the experimental curves obtained are shown in Fig. 1.

The results of our determinations of the solubility of lithium sulfate in water at elevated pressures are given in Table 1 and are shown in Fig. 2 in the form of isotherms expressing the dependence of the solubility of lithium sulfate on

Fig. 2 and Fig. 3: solubility isotherms and isobars of lithium sulfate in water

Figure 2: Fig. 2 and Fig. 3: solubility isotherms and isobars of lithium sulfate in water

pressure at 248, 298, 348, 373, and 388° (preliminary determinations of the dehydration temperatures of $Li_2SO_4 \cdot H_2O$ at various pressures showed that, in the region studied, anhydrous lithium sulfate, and not its crystalline hydrate, is in equilibrium with the saturated solution).

The initial points of the 248, 298, and 348° isotherms show the solubility of lithium sulfate in water in the presence of a vapor phase ([1]).

At pressures equal to the vapor pressures of saturated solutions, the solubility of lithium sulfate in water at temperatures approaching the critical temperature of water becomes very slight, but increases rapidly with increasing pressure.

Thus, for example, at pressures of about one thousand atmospheres, concentrated aqueous solutions of lithium sulfate already exist at temperatures not only approaching the critical temperature of water, but also somewhat exceeding it.

The same significant increase in the solubility of the salt with increasing pressure at temperatures close to the critical temperature of water was observed by us earlier in the sodium sulfate–water system ([5,6]).

The form of the solubility isotherms of lithium sulfate (Fig. 2) changes regularly with increasing temperature. The isotherms at 248 and 298° are convex toward the composition axis. However, already on the isotherm at 348° a convexity toward the pressure axis appears, which with a further increase in temperature (373 and 388°) becomes more sharply expressed.

But at sufficiently high pressures, convexity toward the composition axis also appears on the isotherms at 348, 373, and 388°. The presence of convexity both toward the pressure axis and toward the composition axis causes the appearance of an inflection point.

Fig. 2. Isotherms expressing the dependence of the solubility of lithium sulfate in water on pressure: × –solubility in the presence of a vapor phase. The numbers beside the curves are the temperature in °C

Fig. 3. Isobars expressing the dependence of the solubility of lithium sulfate in water on temperature. × –solubility in the presence of a vapor phase. The numbers beside the curves are the pressure in kg/cm^2

The presence of an inflection point, the tendency of the middle portions of the solubility isotherms, with increasing temperature, to approach the horizontal ever more closely, and the nearly horizontal course of the middle part of the 388° isotherm indicate the proximity of a three-phase region (apparently the upper three-phase region of the system Li_2SO_4—H_2O) with a critical point, to which there should correspond a temperature slightly exceeding 388° and a pressure close to 850 kg/cm^2.

The proximity of the upper three-phase region is apparently also responsible for the intersection of the projections of the solubility isotherms. This intersection indicates that, in the temperature interval studied, the temperature coefficient of solubility of lithium sulfate, negative at relatively low pressures, becomes positive at pressures above 800–850 kg/cm^2.

The change in sign of the temperature coefficient of solubility is also clearly manifested in the course of the solubility isobars (Fig. 3), constructed by interpolating the results obtained.

The features noted above are also characteristic of the sodium sulfate–water system studied by us earlier ([5,6]).

These same features had earlier been found in some systems consisting of organic substances ([7,8]). In all the indicated systems ([5–8]), an upper three-phase region with a critical point was experimentally found, characterized by parameters differing little from

parameters corresponding to a nearly horizontal segment of the solubility isotherms in the fluid phase.

As a result of studying the solubility of lithium sulfate in water in the temperature range 248–388° at various pressures reaching up to $P \sim 1000$ kg/cm^2, it was found that, within the range of parameters investigated, the solubility of lithium sulfate in water at a given temperature increases with increasing pressure, and this increase is especially significant at the highest of the temperatures studied. At pressures below 800–850 kg/cm^2, the temperature coefficient of the solubility of lithium sulfate is negative, while at higher pressures it is positive. With increasing temperature, the form of the solubility isotherms changes regularly: an inflection point appears, and the middle portion of the isotherms approaches the horizontal. The noted features are explained by the proximity of the upper three-phase region.

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Note: Figure translations are in progress. See original paper for figures.