

Summary

The compressibility isotherms of helium have been measured at -70 , -35 , 0 , 50 , 100 and 200° up to 1000 atmospheres pressure.

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THE SYSTEM LITHIUM BROMATE-WATER

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According to A. Potilitzin,¹ crystallization of lithium bromate from aqueous solution results in the formation of a mixture of anhydrous and monohydrate crystals. On the other hand, P. Mylius and R. Funk² are of the opinion that the salt exists only in the anhydrous form. This conflict of opinion seemed to justify further investigation concerning the composition of solid phases which are capable of existence when lithium bromate and water are allowed to come to equilibrium at different temperatures.

Experimental

Preparation of Lithium Bromate.—Lithium bromate was made by bringing together solutions of lithium sulfate and barium bromate, titrating one against the other until a drop of either gave no precipitate. The filtrate from the barium sulfate was concentrated and upon cooling lithium bromate crystallized out. Analysis of the dried salt iodimetrically gave in duplicate analyses 99.50 and 100.0% lithium bromate.

Procedure

All solubility measurements were made by agitating lithium bromate with water in small Pyrex glass-stoppered tubes. Samples of from 0.5 to 1.5 cc. were drawn off by means of pipets into 15-cc. weighing bottles. The solutions were evaporated to dryness and the residues heated to constant weight at 110° .

Two sources of error occur in this method of analysis. The salt may suffer some decomposition during drying and there may be a loss of water by evaporation during the transfer of the solution from the solubility tube to the weighing bottle. These errors were shown to be negligible by the following experiments.

(1) 0.5909 g. of lithium bromate was placed in a weighing bottle, water added, then evaporated and the residue heated at 110° to constant weight. At the end of this treatment the weight of the residue was 0.5912 g.

(2) Water at 75° was transferred to a weighing bottle and allowed to stand exposed to the atmosphere for thirty seconds, during which time

¹ Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **22**, i, 391 (1891).

² Mylius and Funk, *Ber.*, **30**, 1718 (1897).

there was a loss of 1.6 mg. Since ten seconds is the average time for transfer of a sample of solution, it is reasonable to assume that the loss in the case of pure water for this latter interval would be about 0.5 mg. Moreover, the solutions contained about one-third molar quantities of the salt, so that due to this fact evaporation ought to be reduced a further one-third or to about 0.2 mg. It is obvious then that errors due to the above sources may be considered negligible.

In the solubility measurements from 5 to 53° inclusive, automatically controlled water thermostats were used. At the higher temperatures a saturated solution of calcium chloride, covered with a layer of oil, was placed in a 3-liter beaker. The latter was placed in an oven heated by gas and controlled by hand, served as a thermostat. The calcium chloride solution and the system being studied were stirred by wind turbines until equilibrium was attained. The lower temperatures were maintained constant within 0.02° and the higher within 0.10°. Equilibrium appeared to be reached quickly, usually in about three hours. The metastable

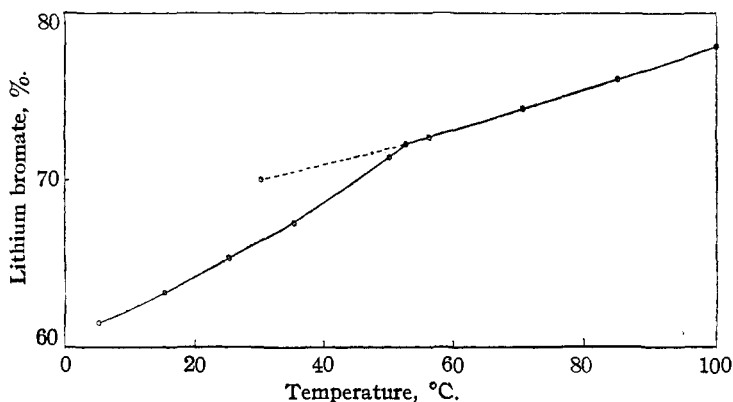


Fig. 1.—Solubility of lithium bromate in water.

point shown on the curve at 30° was obtained by allowing a solution saturated at 100° to cool to 30° over a period of eight hours. This solution was kept at 30° for four hours without stirring and then analyzed. The point so obtained fell so well on a continuation of the anhydrous curve that it is reasonably certain that it is very close to the true value.

The results of these measurements are given in the table and when plotted the curve of Fig. 1 is obtained.

Temp., °C.	% LiBrO ₃	Temp., °C.	% LiBrO ₃
5	61.6	53	72.4
15	63.3	56	72.6
25	65.4	70.5	74.3
35	67.5	85	76.2
50	71.5	100	78.0

An inspection of the curve in Fig. 1 shows a distinct break at about 52° and proves the existence of at least two solid phases. These results were obtained from the undersaturated side only as the salt showed a great tendency to form supersaturated solutions.

To determine the composition of the solid phases, moist crystals which had come out of solution at room temperature were placed in a desiccator with anhydrous lithium bromate until no further loss was observed. Analysis of this material showed 0.995 and 1.008 molecules of water to one molecule of lithium bromate, in other words, the monohydrate. Crystals grown at 55° were small brilliant pyramids and upon analysis proved to be anhydrous lithium bromate. It is therefore evident that the two solid phases involved in this system are lithium bromate monohydrate, which is stable below 52° , and anhydrous lithium bromate stable above this temperature.

The determination of the transition point of lithium bromate-lithium bromate monohydrate was also made by cooling a solution saturated at 80° and, although supersaturation gave some difficulty, a number of results were obtained which gave an average figure of 50.8° . The agreement between this value and the one obtained by the solubility method may be considered good in view of the great viscosity of the solutions, the slight increase in solubility of the anhydrous lithium bromate with increase in temperature, and the marked tendency to form supersaturated solutions.

Attempts to determine the melting point of anhydrous lithium bromate by direct measurement gave an average of 248° . This, however, is low as some decomposition was observed. Extrapolation of the solubility curve indicated a melting point of 260° .

Summary

1. The solubility of lithium bromate in water has been determined over the range of temperature $5-100^{\circ}$.
2. Lithium bromate may exist in contact with its aqueous solutions as the monohydrate or as anhydrous salt.
3. The transition temperature lies between 50.8 and 52° .
4. The melting point of anhydrous lithium bromate lies between 248 and approximately 260° .

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