The Solubility Curves of Boric Acid and the Borates of Sodium

By Walter C. Blasdale and Cyril M. Slansky

A study of the system sodium oxide–boric oxide–water between 0 and 100° was begun in this Laboratory several years ago and is not yet completed. This study necessitated extension and revision of the published data relating to the solubilities of boric acid and the sodium salts concerned, in the absence of an excess of either sodium or boric oxide. The results of this part of the work are reported in the present paper.

The solid phases concerned include the only known hydrate of boric oxide, commonly sold as boric acid, which is stable between the cryohydric point and the boiling point of the saturated solution. The sodium salts include a pentaborate (NaB₅O₈·5H₂O), three hydrates of sodium tetraborate with ten, five and four molecules of water, respectively, and two hydrates of sodium metaborate with four and two molecules of water. A still more basic borate can be prepared but only from solutions containing a larger proportion of sodium oxide than its formula requires. References to additional hydrates are to be found, especially in the earlier literature, but the evidence for their existence is not convincing.

Experimental Work.—The different solid phases used were prepared from the purest obtainable boric acid, sodium tetraborate decahydrate and sodium hydroxide. They were enclosed in rubber-stoppered, Pyrex flasks with the proper amount of water and agitated in either a water or an oil-bath whose temperature was kept to within 0.2° by means of a heating coil and a sensitive mercury-filled regulator, until saturated. The temperature of the bath was determined by means of mercury thermometers calibrated by the Bureau of Standards. Samples

of the resulting solutions were removed at twenty-four hour intervals by means of a filtering pipet and delivered into weighing bottles. The weighed samples were diluted and titrated, first with 0.5 N hydrochloric acid and either methyl orange or methyl red, and then with 0.25 N sodium hydroxide using phenolphthalein and an excess of mannite. The sum of the sodium oxide found by the first titration and the boric oxide found by
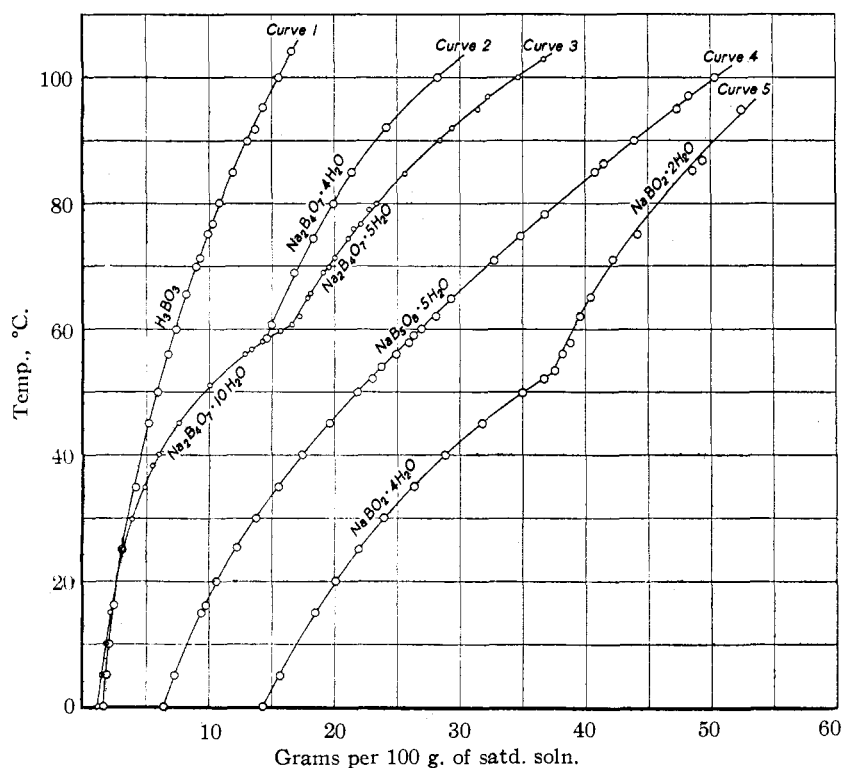

Fig. 1.

the second gave the total amount of dissolved solid present. For the saturation of solutions at the boiling point a special flask, similar to that used for measuring the boiling point temperature, but of greater capacity, was devised.

The Solubility Curve for Boric Acid.—The solid used was purified by two recrystallizations and the solubilities at approximately 5° intervals determined. The relations of solubility, expressed as weight of boric oxide per hundred parts of saturated solution, to temperature were plotted on a large scale, which is reproduced as Curve I

of Fig. 1. The values for the solubility at intervals of exactly 5°, derived from this curve, appear in column 2 of Table I. Fifteen points on this solubility curve between −0.74 and 120° have been determined previously by Nasini and Ageno.[1] Their results are in good agreement with those obtained by us.

TABLE I

SOLUBILITIES EXPRESSED IN GRAMS OF ANHYDROUS SOLIDS PER 100 GRAMS OF SATURATED SOLUTION

Temp., °C.	Boric acid, g. B_2O_3	Sodium tetraborate, g. $Na_2B_4O_7$	Sodium penta-borate, g. NaB_5O_8	Sodium meta-borate, g. $NaBO_2$
0	1.52	1.18	6.28	14.10
5	1.77	1.44	7.10	15.70
10	1.98	1.76	8.10	17.23
15	2.35	2.12	9.30	18.50
20	2.62	2.58	10.55	20.22
25	3.06	3.13	12.20	22.00
30	3.57	3.85	13.75	23.90
35	4.05	4.76	15.60	26.22
40	4.60	6.00	17.40	28.75
45	5.25	7.58	19.63	31.81
50	5.76	9.55	21.80	35.02
54[a]				37.85
55	6.50	12.25	24.30	38.12
58.5[a]		14.52	Kernite	
60	7.30		14.82	26.90	39.00
60.8[a]		16.65		
65	8.12	17.88	15.88	29.35	40.35
70	8.87	19.49	17.12	32.25	41.90
75	9.80	21.30	18.41	34.98	43.80
80	10.73	23.38	19.88	37.84	45.80
85	11.83	25.73	21.48	40.77	48.10
90	13.10	28.37	23.31	43.80	50.35
95	14.20	31.28	25.55	47.05	52.80
100	15.50	34.63	28.22	50.30	55.60
102.8[b]		36.73		
103.3[b]	16.48			

[a] Transition points.   [b] Boiling points.

The Curves for Sodium Tetraborate.—No difficulty was experienced in preparing a solid corresponding closely to the formula of the decahydrate by vigorously agitating solutions saturated at 55° while they cooled to 20°, filtering the resulting crystalline granules on a Büchner filter, washing with dilute alcohol of increasing concentrations and allowing to dry at 25°. The corresponding pentahydrate was made by allowing solutions saturated at 80° to cool to 60° and treating the separated product similarly. The resulting solubility determinations, in which either the deca or the pentahydrates were used as solid phases, are plotted on curve 3 of the figure and the interpolated values for 5° intervals appear in

(1) R. Nasini and I. Ageno, Z. physik. Chem., **69**, 484 (1909).

column 3 and column 4 (kernite) of the table. The large number of determinations in the neighborhood of the transition temperature ($10H_2O \longleftrightarrow 5H_2O$) fix the value of this temperature at 60.8° to within 0.2°. This value was confirmed by heating a mass of the decahydrate at a nearly uniform rate and plotting the rise in temperature against time. Eighteen points on this solubility curve were determined by W. D. Horne and Elizabeth Van Wagner,[2] who made use of a bath whose temperature was not automatically controlled. Although many of their results are in good agreement with ours, they indicate a break in the continuity of the curve at 60° instead of 60.8°.

The data obtained using the deca and pentahydrates as solid phases, even up to 100°, gave no indication of the formation of a stable tetrahydrate. This salt constitutes the mineral kernite, which occurs as a deeply-buried deposit of enormous extent in Kern County, California. Its crystallography, optical properties and mineral associations have been described by Schaller.[3]

As this deposit represents the only known occurrence of the tetrahydrate, the conditions which determine its formation and stability constitute an interesting problem. Schaller was unable[3a] to cause it to separate from solutions up to 100° and found that when kernite was added to a saturated solution at room temperature it rapidly changed over into the decahydrate. He also noted the frequent occurrence of thin layers of the pentahydrate on and along cleavage cracks of kernite which had been exposed to ordinary atmospheric conditions. He quotes the result of an experiment by R. C. Wells of the Geological Survey, in which borax was heated to 150° for several days in a sealed tube of such a shape that some of the water condensed to liquid in the bent uppermost part of the tube, which gave rise to almost pure kernite. Schaller concluded therefore that the range of stability of the tetrahydrate was around 150°. This conclusion has been challenged by Menzel, Schulz and Deckert[4] who

(2) W. D. Horne and Elizabeth Van Wagner, Am. Chem. J., **30**, 347 (1903).

(3) W. T. Schaller, Professional Paper 158, U. S. Geological Survey, 1930, pp. 137–170, and Bulletin 871, U. S. Geological Survey, 1936, pp. 99–105.

(3a) Since then Schaller has obtained crystals of kernite several millimeters long, without seeding, from a saturated solution of sodium tetraborate, at 92°, by very slow evaporation (personal communication from Schaller).

(4) Menzel, Schulz and Deckert, Naturwissenschaften, **23**, 832 (1935).

found it possible to obtain constant values for five points on the solubility curve of kernite between 60 and 100° all of which represented lower concentrations of sodium tetraborate than those found for the pentahydrate at corresponding temperatures. These workers also synthesized kernite by heating partially dehydrated decahydrate in a closed tube at 130–140° and, at a very much slower rate, at 100°. From their solubility data they estimated that there was a transition point ($10H_2O \longleftrightarrow 4H_2O$) at 57.5° and that the pentahydrate was metastable, in contact with aqueous solutions between 0 and 100°.

In our study of this question we were fortunate in being able to obtain from Professor Frank H. Probert, Dean of the College of Mines, a supply of remarkably pure kernite. It gave no tests for chlorides, carbonates or sulfates and very nearly the theoretical percentage of water. Using it as a solid phase we were able to obtain constant values for its solubility, which are plotted on curve 2 of the figure. This curve cuts that of the decahydrate at 58.5°. We were also able to show that a solution saturated with the pentahydrate at 94.5° changed during the course of five days from 30.9 to 27.05% of sodium tetraborate, which is not greatly in excess of the value found for the tetrahydrate at this temperature. At 60° a corresponding but very much slower change was found. We are compelled to conclude therefore that although the pentahydrate possesses a remarkable degree of stability between 60.2 and 100°, it is thermodynamically metastable, with respect to the tetrahydrate, within these limits. We have also been able to prepare kernite by heating the pentahydrate in a sealed tube, the lower end of which was kept in a furnace heated from 130 to 150° for a period of three weeks.

The Solubility Curve of Sodium Pentaborate.—This compound exhibits a remarkable ability to form supersaturated solutions, and when a solid finally separates it takes the form of a dense crust, of aggregate crystals, in which boric oxide is present in excess of that demanded by the accepted formula, namely, $NaB_5O_8\cdot5H_2O$. The best method of preparation we have discovered is to make a solution saturated at 75° (170 g. $Na_2B_4O_7\cdot10H_2O$, 170 g. H_3BO_3, 700 g. H_2O) allow to cool to 60°, inoculate with a previously prepared sample of pentaborate and allow to cool to 25° with vigorous and constant agitation. This results in the gradual separation of small granules, which

lack definite bounding planes but, under the microscope, behave like homogeneous structures. When the separated product was treated with absolute alcohol, appreciable amounts of boric acid were dissolved out. As it was also shown that the solubility of the pentaborate in absolute alcohol was negligible, the preparations used by us were digested with double their bulk of absolute alcohol for about six hours, after separation on a Büchner funnel.

Analysis of two such preparations gave the following results:

	Pure pentaborate	Preparation, L	Preparation, O
Na_2O	10.50	10.44	10.56
B_2O_3	58.98	59.20	59.06
H_2O	30.52	30.67	30.59

The frequent associations of boric acid and borax with the separated pentaborate has led to the suggestion by Rosenheim and Leyser[5] that the pentaborate ceases to be stable with respect to a mixture of boric acid and borax, at temperatures below normal. In order to test this matter the solubility of the pentaborate in the presence of boric acid and of borax, respectively, at temperatures of 25, 20, 16.1 and 10° was determined. It was found possible to prepare solutions saturated as to pentaborate and either boric acid or borax at all four temperatures. The results of the analyses of these solutions are given in Table II.

TABLE II

Composition of Solutions, Expressed in Grams of Sodium Oxide and Boric Oxide, per 100 G. of Saturated Solutions

Solid phases	Pentaborate + boric acid		Pentaborate		Pentaborate + borax	
	Na_2O	B_2O_3	Na_2O	B_2O_3	Na_2O	B_2O_3
25°	1.62	10.08	1.83	10.32	2.82	12.70
20°	1.46	8.68	1.60	8.90	2.19	10.37
16.1°	1.34	7.94	1.46	8.11	1.88	9.09
10°	1.22	6.95	1.18	7.32	1.66	7.98

When the composition of these solutions was plotted, using sodium oxide and boric oxide as coördinates, it was obvious that the lengths of the intervals over which the pentaborate existed as a stable solid phase decreased with decreasing temperature, also that the composition of the solutions congruently saturated as to pentaborate was much nearer that of solutions saturated as to pentaborate and boric acid than those saturated as to pentaborate and borax. By extrapolation it was estimated that the pentaborate became metastable with respect to its congruently saturated

(5) Rosenheim and Leyser, Z. anorg. allgem. Chem., 119, 1 (1921).

solutions at about 2° but was stable much below this temperature in the presence of a slight excess of sodium oxide.

The solubility curve of the pentaborate, curve four of the figure, shows no unusual features. There is no evidence of the formation of a lower hydrate, even at the boiling point of the solutions; furthermore, it was found that the solid could be heated in an open weighing bottle to 70° without appreciable loss. Heated to 116° it gradually formed a viscous liquid and began to lose water. At a still higher temperature it, like boric acid, loses boric oxide also.

The Solubility Curve of Sodium Metaborate.— The tetrahydrate of this salt is easily prepared in the form of well-developed crystals of almost any desired size. If separated from congruently saturated solutions below 50° their composition agrees closely with the theoretical value. The dihydrate is more difficult to prepare in the form of well formed crystals but the tetrahydrate readily changes into the dihydrate above 60°. Both solids form solutions which are greatly supersaturated; those saturated above 70° are extremely viscous and assume a glass-like character similar to solutions of sodium silicate. This viscosity greatly delays the attainment of equilibrium in either undersaturated or supersaturated solutions and makes filtration very difficult. On account of these difficulties the solubility values found for temperatures in excess of 80° are less accurate than those obtained for the rest of the curve. It was not possible to fix the value of the boiling point or the composition of solution saturated at this temperature. The results, plotted as curve five of the figure, fix the value of the transition temperature $(4H_2O \longleftrightarrow 2H_2O)$ at 54°. This value was confirmed by heating the tetrahydrate at a constant rate and plotting the temperature–time relation.

Summary of Results

1. The solubilities of boric acid; of the deca-, penta- and tetra-hydrates of sodium tetraborate; of the tetra- and dihydrate of sodium metaborate and of sodium pentaborate have been determined and the values for 5° intervals between 0 and 100° tabulated.

2. The metastable transition temperature $(10H_2O \longleftrightarrow 5H_2O)$ of sodium tetraborate has been fixed at 60.8° and the stable transition temperature $(10H_2O \longleftrightarrow 4H_2O)$ of the same salt has been fixed at 58.5°. The stable transition temperature $(4H_2O \longleftrightarrow 2H_2O)$ of sodium metaborate has been fixed at 54°.

3. Evidence is given that the pentahydrate of sodium pentaborate is stable in contact with its congruently saturated solutions between 10 and 100°, and at still lower temperatures in contact with solutions containing a slight excess of sodium oxide.

The Solubility of Mercuric Chloride in Aqueous Solutions of Several Chlorides

BY HENRY C. THOMAS

The solubility of mercuric chloride in aqueous chloride solutions has been the subject of many investigations[1-10] since J. Davy[11] first noted in 1822 the extraordinary solubility of this compound in hydrochloric acid. It has been thought worth while to repeat and extend some of the earlier work in order to obtain solubilities of sufficient accuracy to clear the way for further ideas on the nature of these complex solutions.

Experimental

J. T. Baker "Analyzed" chemicals were used without further purification. Solutions were prepared with chloride-free distilled water.

Concentrated stock solutions of the solute salts were analyzed gravimetrically for their chloride content. At least five analyses were made on each solution, the results of which agreed to within 0.05%. Solutions for the individual solubility determinations were prepared by weight dilution of the stock chloride solutions. The more concentrated solutions containing hydrochloric acid were

(1) HCl: Engel, Ann. chim. phys., **17**, 338 (1889).

(2) CsCl: Foote, Am. Chem. J., **30**, 339 (1903).

(3) BaCl₂: Foote and Bristol, ibid., **32**, 246 (1904).

(4) NaCl, KCl, RbCl: Foote and Levy, ibid., **35**, 239 (1906).

(5) KCl: Tichomirov, J. Russ. Phys.-Chem. Soc., **39**, 731 (1907).

(6) NH₄Cl: Meerburg, Z. anorg. allgem. Chem., **59**, 136 (1908).

(7) BaCl₂: Schreinemakers, Chem. Weekblad, **7**, 197 (1910).

(8) CuCl₂: Schreinemakers and Thonus, Proc. Roy. Acad. Sci. Amst., **15**, 472 (1912).

(9) LiCl, NaCl, KCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂: Herz and Paul, Z. anorg. allgem. Chem., **82**, 431 (1913).

(10) KCl: Tourneux, Ann. chim. phys., **11**, 225 (1919).

(11) J. Davy, Phil. Trans., **112**, 359 (1822).