Figure 1 shows that at high pressures the solubility of carbon dioxide increases with an increase in temperature. This characteristic, encountered at high pressures, is not widely known because such conditions are uncommon and seldom met with in ordinary activity.

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Solubility of Some Mixtures of Alkali Borates

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Measurements were made of the solubility relationships of various combinations of sodium pentaborate and diborate, ammonium pentaborate, tetraborate and diborate, and potassium pentaborate and diborate, in water at 20° C, 30°, and 40° C.

It was demonstrated that the solubility peaks in these mixed systems are controlled by pH. The narrow composition limits governing the solubility peak in the sodium oxide-boric system can be greatly widened by the addition of ammonium ion.

Boric acid and sodium borates have been used as timber preservatives since 1939 (2). Recent developments of the impregnation process (4) have required the formulation of aqueous solutions of maximum boric oxide solubility in the pH range 6 to 8. The present work takes the obvious approach of using mixtures of various alkali borates. Economic considerations limit interest in such systems to sodium oxide, potassium oxide, ammonium oxide, boric oxide, and water, and solubility relationships have now been established for the most concentrated boric oxide solutions in this restricted pH range.

The system sodium oxide-boric oxide-water has been investigated at 30° C. by Dukelski (3), at 0° C. by Rosenheim and Leyser (7), and over the range 0° to 90° C. by Sborgi (8). In addition, the solubilities of boric acid and the various sodium borates in water have been measured by Blasdale and Slansky (1). In Dukelski's paper the system potassium oxide-boric oxide-water at 30° C. is also described, and Sborgi and Ferri (9) have investigated the system ammonium oxide-boric oxide-water from 0° to 90° C. Apart from a few values for the solubility of sodium diborate with ammonium diborate given by Sborgi and Gallichi (10), no references have been found to work done on the mixed systems.

In the present work, solubility measurements were made by prolonged shaking of solid phases with water, employing those solid phases stable in equilibrium with the final solution. This has the advantage of ensuring that supersaturation cannot take place (provided the temperature is not at any stage allowed to rise above the final temperature), and it also enables equilibrium to be established relatively quickly. Any desired point on the solubility curve can be obtained by restricting the amount of one or more constituents, and thus the steep portions of the curve, where solubility relationships are changing rapidly with minor changes in composition, can be explored fully.

A constant-temperature room was used, controlled to ±0.2° C. While such a room is not as accurate as a water bath, it has considerable advantages when samples are withdrawn for filtration, or measurement of pH and density.

EXPERIMENTAL

In each solubility determination, 20 ml. of water was shaken with weighed amounts of the various desired solid phases stable in equilibrium with the final solution. Shaking was continued for approximately 4 days. The solutions were allowed to settle and then filtered rapidly through Whatman No. 41 paper. If the solutions were not quickly filtered and covered, the low humidity of the room caused evaporation and cooling. With the technique described, no lowering of temperature was observed. Immediately after filtration the room temperature was raised about 1° C. to avoid any possible crystallization. A 10-ml. sample was withdrawn in a calibrated pipet and weighed in a dry 100-ml. flask, which was afterwards made up to volume, thus combining density measurement with subsequent dilution of a sample for analysis. The pH of the concentrated solution was measured on a glass electrode system at the working temperature.

TABLE I. CHARACTERISTICS OF MIXTURES OF ALKALI BORATES AT 20° ± 0.2° C.

Solids Shaken with 20 Ml. of Water, Grams								Composition of Saturated Solution. Wt. %				pH at 20° C.	Density at 20° C.
Sodium pentaborate 1:5:10	Sodium diborate 1:2:10	Boric acid	Ammonium pentaborate 1:5:8	Ammonium diborate 1:2:4	Ammonium solution 0.880	Potassium pentaborate 1:5:8	Potassium diborate 1:2:5	Na_2O	$(NH_4)_2O$	K_2O	B_2O_3		
6 (Ex)[a]	2 (Ex)	..	..	..	..	..	..	2.23	..	..	10.4	7.15	1.096
..	..	..	3 (Ex)	4 (Ex)	..	..	..	..	2.54	..	10.4	8.27	1.081
..	..	..	..	..	..	6 (Ex)	8 (Ex)	..	..	4.00	7.0	9.17	1.088
6	2	..	3	4	..	..	..	1.33	1.95	..	13.5	7.88	1.118
6	2	..	..	..	..	6	8	0.90	..	0.80	4.8	8.44	1.053
..	..	..	3	4	..	6	8	..	2.06	2.80	11.5	8.91	1.121
6	2	..	3	4	..	6	8	0.92	2.28	3.55	15.5	9.05	1.173
6	0.4	..	..	..	..	..	..	1.91	..	..	9.8	7.00	1.087
6	0.2	..	..	..	..	..	..	1.73	..	..	9.4	6.86	1.082
2	2	..	..	..	..	..	..	1.43	..	..	6.4	7.60	1.058
0.5	2	..	..	..	..	..	..	0.85	..	..	2.7	8.60	1.026
1	..	2 (Ex)	..	..	..	..	..	0.48	..	..	4.7	6.33	1.035
6	2	..	3	1.2	..	..	..	1.96	0.86	..	13.2	7.32	1.118
6	2	..	3	0.6	..	..	..	2.23	0.74	..	13.8	7.20	1.124
6	2	..	3	..	..	..	..	2.21	0.72	..	13.7	7.20	1.124
6	2	..	1	4	..	..	..	1.33	1.96	..	13.8	7.88	1.122
6	2	..	0.5	4	..	..	..	1.31	1.94	..	13.8	7.90	1.121
6	2	..	..	4	..	..	..	1.28	1.91	..	13.5	7.92	1.118
6	2	..	..	..	0.40	..	..	2.14	0.70	..	12.9	7.25	1.117
6	2	..	..	..	0.20	..	..	2.20	0.39	..	12.0	7.15	1.111
6	0.4	..	3	4	..	..	..	1.32	1.95	..	13.7	7.84	1.119
6	0.4	..	3	..	..	..	..	1.86	0.60	..	12.4	7.04	1.107
6	0.4	..	..	4	..	..	..	1.32	2.01	..	13.9	7.90	1.122
2	2	..	3	4	..	..	..	1.03	2.66	..	13.8	8.22	1.124
2	2	..	3	..	..	..	..	1.74	1.06	..	12.8	7.44	1.114
2	2	..	..	4	..	..	..	0.94	2.33	..	11.4	8.51	1.101
6	2	..	3	4	..	6	..	1.19	1.98	0.12	13.3	8.00	1.116
6	2	..	3	..	..	6	..	2.15	0.47	0.07	12.7	7.16	1.114
6	2	..	..	..	..	6	..	2.18	..	0.11	10.7	7.15	1.099

[a] (Ex) denotes sufficient excess present to leave solid phase in final solution.

TABLE II. CHARACTERISTICS OF MIXTURES OF ALKALI BORATES AT 30° ± 0.2° C.

Solids Shaken with 20 Ml. of Water, Grams							Composition of Saturated Solution, Wt. %				pH at 30^{a} C.	Density at 30° C.
Sodium pentaborate 1:5:10	Sodium diborate 1:2:10	Ammonium pentaborate 1:5:8	Ammonium diborate 1:2:4	Ammonium solution 0.880	Potassium pentaborate 1:5:8	Potassium diborate 1:2:5	Na_2O	$(NH_4)_2O$	K_2O	B_2O_3		
9 (Ex)[a]	6(Ex)	..	..	..	..	..	3.59	..	..	15.8	7.03	1.156
..	..	6 (Ex)	5 (Ex)	..	..	..	..	3.51	..	13.9	8.18	1.084
..	..	..	..	..	7 (Ex)	8 (Ex)	..	..	7.20	12.9	8.96	1.187
9	6	6	5	..	..	..	2.56	2.43	..	20.2	7.63	1.191
9	6	..	..	..	7	8	1.33	..	4.55	12.0	8.82	1.148
..	..	6	5	..	7	8	..	2.28	4.00	16.2	8.59	1.181
9	6	6	5	..	7	8	1.71	3.18	2.05	20.7	8.41	1.216
9	1	..	..	..	..	..	2.79	..	..	13.5	6.81	1.126
9	0.5	..	..	..	..	..	2.46	..	..	13.0	6.66	1.115
3	6	..	..	..	..	..	2.25	..	..	9.4	7.63	1.088
9	6	6	2	..	..	..	2.65	2.37	..	20.1	7.56	1.191
9	6	6	1	..	..	..	3.54	1.21	..	20.4	7.11	1.199
9	6	6	..	..	..	..	3.58	1.11	..	20.6	7.12	1.199
9	6	2	5	..	..	..	2.58	2.40	..	20.3	7.63	1.193
9	6	1	5	..	..	..	2.56	2.50	..	20.1	7.62	1.192
9	6	..	5	..	..	..	2.52	2.47	..	20.0	7.62	1.190
9	1	6	5	..	..	..	2.56	2.34	..	19.9	7.63	1.188
9	1	6	..	..	..	..	2.21	0.73	..	15.2	6.67	1.133
9	1	..	5	..	..	..	2.66	2.20	..	20.0	7.62	1.184
3	6	6	5	..	..	..	2.06	3.03	..	19.2	7.93	1.180
3	6	12	..	..	..	..	3.39	1.41	..	20.1	7.21	1.193
3	6	..	10	..	..	..	1.61	3.34	..	16.1	8.40	1.152
..	6	6	5	..	..	..	1.81	3.70	..	19.8	8.26	1.216
11	7	..	..	1.45	..	..	2.58	2.12	..	19.4	7.53	1.178
11	7	..	..	1.16	..	..	2.96	1.53	..	19.0	7.36	1.179
11	7	..	..	0.87	..	..	3.61	1.09	..	19.8	7.13	1.189
11	7	..	..	0.58	..	..	3.60	0.76	..	18.1	7.08	1.180
11	7	..	..	0.29	..	..	3.60	0.43	..	18.8	7.06	1.166

[a] (Ex) denotes sufficient excess present to leave solid phase in final solution.

After dilution, the boric acid and total alkalies were titrated by the mannitol method, sodium and potassium were determined by flame photometer, and ammonia was distilled and determined by Kjeldahl's method. The total alkali as determined by titration always showed excellent agreement with the sum of the figures for sodium, potassium, and ammonium.

PREPARATION OF BORATES

Nomenclature: The nomenclature of borates is in a confused state (5); this is made worse by the common usage of "sodium tetraborate" for borax. Accordingly, the following nomenclature is used in this paper (based on the Berzelian formulas):

1:2 borate.	Diborate – e.g., $Na_2O.2B_2O_3$
1:4 borate.	Tetraborate – e.g., $Na_2O.4B_2O_3$
1:5 borate.	Pentaborate – e.g., $Na_2O.5B_2O_3$

Boric Acid. Hopkin and Williams Analar boric acid (H_3BO_3) was used.

Sodium Pentaborate. Some difficulty was experienced in preparing the pure compound, owing to the narrow range of solution composition where pentaborate crystallizes alone. The method of preparation quoted by Blasdale and Slansky (1) was not tried.

A satisfactory method found by experiment was to dissolve 327 grams of boric acid and 47.8 grams of sodium hydroxide in 400 ml. of hot water and crystallize at room temperature, after seeding with a previously prepared crystal. A solid crust of pentaborate was invariably obtained within 12 hours; but after prolonged standing a second crop of finely divided crystals containing excess boric oxide was obtained. Only the first crop, whose composition always came near the figure shown, was used.

	Theoretical $Na_2O.5B_2O_3.10H_2O$, %	Typical Preparation, %
Na_2O	10.5	10.2
B_2O_3	59.1	58.3

Sodium Diborate (borax): British Drug Houses Analar borax was used $NA_2O.2B_2O_3.10H2O$.

Ammonium pentaborate was prepared by heating together 400 grams of boric acid, 160 ml. of ammonia solution (specific gravity, 0.880), 550 ml. of water, and crystallizing at room temperature.

	Theoretical $(NH_4)_2O.5B_2O_3.8H_2O$, %	Typical Preparation, %
$(NH_4)_2O$	9.6	9.6
B_2O_3	64.0	64.9

Ammonium Tetraborate. According to Sborgi and Ferri (9) this salt is stable only at temperatures higher than 31° C. To prepare it, 121 grams of boric acid, 43 ml. of 0.880 ammonia solution, and 160 ml. of water were boiled and allowed to crystallize in an oven at 60° C. The salt was kept in an incubator at 37° C. until used.

	Theoretical $(NH_4)_2O.4B_2O_3.6H_2O$, %	Typical Preparation, %
$(NH_4)_2O$	11.9	12.0
B_2O_3	63.5	65.5

Ammonium diborate was prepared by heating together 210 grams of boric acid, 300 ml. of 0.880 ammonia solution, and 400 ml. of water and allowing it to crystallize in a refrigerator at 5° C.

	Theoretical $(NH_4)_2O.2B_2O_3.4H_2O$, %	Typical Preparation, %
$(NH_4)_2O$	19.8	20.5
B_2O_3	52.8	54.2

Potassium pentaborate was prepared by heating 160 grams of boric acid, 30 grams of potassium hydroxide, and 800 ml. of water, and allowing it to crystallize in a refrigerator at 5° C.

	Theoretical $K_2O.5B_2O_3.8H_2O$, %	Typical Preparation, %
K_2O	16.0	16.2
B_2O_3	59.5	58.9

Potassium diborate was prepared by heating 175 grams of boric acid, 135 grams of potassium hydroxide, and 180 ml. of water and allowing it to crystallize for 3 days in a refrigerator at 5° C.

	Theoretical $K_2O.2B_2O_3.5H_2O$, %	Typical Preparation, %
K_2O	29.1	29.2
B_2O_3	43.1	43.0

TABLE III. CHARACTERISTICS OF MIXTURES OF ALKALI BORATES AT 40° ± 0.2° C.

Solids Shaken with 20 Ml. of Water, Grams								Composition of Saturated Solution, Wt. %					
Sodium pentaborate 1:5:10	Sodium diborate 1:2:10	Ammonium pentaborate 1:5:8	Ammonium tetraborate 1:4:6	Ammonium diborate 1:2:4	Ammonia solution 0.880	Potassium pentaborate 1:5:8	Potassium diborate 1:2:5	Na_2O	$(NH_4)_2O$	K_2O	B_2O_3	pH at 40° C.	Density at 40° C.
13 (Ex)[a]	11 (Ex)	..	..	..	..	..	..	5.89	..	..	23.6	7.02	1.246
..	..	..	6 (Ex)	7 (Ex)	..	..	..	..	4.63	..	17.8	8.05	1.142
..	..	..	..	..	..	25 (Ex)	21 (Ex)	..	..	9.90	17.7	8.86	1.237
13	11	..	6	7	..	..	..	4.63	3.00	..	28.5	7.46	1.284
13	11	..	..	..	..	25	21	2.27	..	9.90	24.6	8.80	1.360
..	..	..	6	7	..	25	21	..	3.67	9.35	28.2	8.61	1.349
13	11	..	6	7	..	25	21	2.88	3.06	6.80	30.1	8.40	1.374
13	2	..	..	..	..	..	..	3.83	..	..	18.4	6.65	1.172
13	0.5	..	..	..	..	..	..	3.10	..	..	16.3	6.35	1.142
4	11	..	..	..	..	..	..	3.43	..	..	12.9	7.80	1.125
13	11	..	6	3	..	..	..	5.44	2.36	..	30.0	7.32	1.312
13	11	..	6	1	..	..	..	5.94	1.89	..	30.6	7.27	1.326
13	11	..	6	..	..	..	..	5.98	1.63	..	30.0	7.08	1.319
13	11	..	2	7	..	..	..	4.47	3.09	..	28.0	7.57	1.285
13	11	..	1	7	..	..	..	4.38	3.05	..	27.6	7.57	1.277
13	11	..	..	7	..	..	..	4.43	2.98	..	28.3	7.54	1.285
13	11	10	..	..	..	..	..	5.39	1.68	..	28.3	7.10	1.296
13	11	..	..	..	0.35	..	..	5.76	0.47	..	24.9	7.11	1.258
13	2	..	6	7	..	..	..	4.28	2.85	..	27.4	7.37	1.271
13	2	..	6	..	..	..	..	4.00	1.20	..	23.4	6.83	1.220
13	2	..	..	7	..	..	..	4.23	3.06	..	28.1	7.43	1.275
4	11	..	6	7	..	..	..	3.46	4.78	..	28.3	8.01	1.286
4	11	..	10	..	..	..	..	4.43	3.11	..	28.4	7.52	1.289
4	11	..	..	10	..	..	..	2.78	4.36	..	22.6	8.39	1.222

[a] (Ex) denotes sufficient excess present to leave solid phase in final solution.

RESULTS

Table I shows the solubilities of mixtures of borates in water at 20° ± 0.2° C. Also included are the results of two experiments in which 0.880 ammonia was used in the place of the ammonium salts. Tables II and III show solubilities at 30° and 40° C.

The present work is best compared with that of previous investigators by graphing the results; this has been done in Figure I for part of the sodium oxide-boric oxide system at 20° C.

DISCUSSION

A study of the published figures for the boric acid-sodium borate system reveals that the solubilities vary greatly with the ratio of sodium oxide to boric oxide. In particular, there is a large solubility peak in the region between the pentaborate and the diborate. Thus Blasdale and Slansky (1) quote the composition of the saturated solutions at 20° C. as follows:

Molecular Ratio	Na_2O, Wt. %	B_2O_3, Wt. %
B_2O_3	..	2.62
$Na_2O:5B_2O_3$	1.60	8.90
$Na_2O:4.22B_2O_3$	2.19	10.37
$Na_2O:2B_2O_3$	0.80	1.78

The composition limits for this solubility peak are exceedingly narrow, particularly on the diborate side (3).

The measurements made by Sborgi and Ferri (9) show a similar solubility peak between ammonium pentaborate and ammonium diborate at 20° C.; and above 31° C. the same solubility peak is found for ammonium diborate and ammonium tetraborate, which latter replaces ammonium pentaborate as the stable phase at these temperatures. Dukelski (3) found a similar peak between potassium pentaborate and diborate at 30° C.

The first point of interest emerging from the present results is the molecular ratio for peak solubility, with its consequent effect on pH. Considering each alkali separately, it can be seen that the molecular ratio of alkali to boric oxide at which peak solubility occurs, varies with temperature. Table IV summarizes these solubility peaks.

The solubility relationships between the mixed alkali borates are more complex. Thus the first seven experiments in Table I show the peak solubilities for the various alkali borates singly and in combination, at 20° C. The values for boric oxide solubility emphasize the significance of pH. The sodium and ammonium solubility peaks are at pH values of 7.15 and 8.27, respectively, and a mixture of the two alkalies gives an intermediate pH (7.88) with an enhanced boric oxide solubility. The total solids content of the saturated solution is also increased, although the individual solubilities of sodium and ammonium ions are lowered. With sodium and potassium, however, the pH values of the individual peak solubilities are so far apart that the pH of the mixed alkali borates falls at 8.44, a point of low solubility for the sodium borate system and for the potassium borate system. The mixed sodium-potassium system thus has a lower boric oxide solubility than either alkali taken separately.

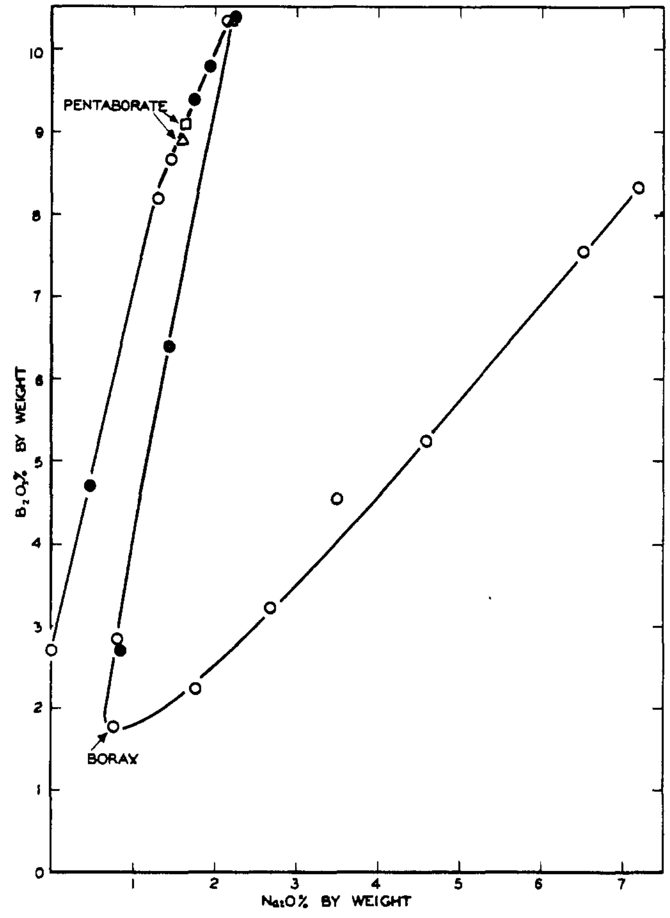

Figure 1. System boric oxide – sodium oxide – water at 20° C.

○ Sborgi (8)
△ Blasdale and Slansky (1)
□ Rollet and Peng (6)
● Experimental

When ammonium and potassium borates are mixed, the pH values are closer, and the solubility is increased in respect to both boric oxide content and total solids, while the solubilities of ammonium and potassium ions are reduced below the peak values of the individual alkali systems.

TABLE IV. MOLECULAR COMPOSITION FOR PEAK SOLUBILITY

Temp., ° C.	Sodium Diborate and Pentaborate		Ammonium Diborate and Pentaborate		Ammonium Diborate and Tetraborate		Potassium Diborate and Pentaborate	
	$Na_2O:B_2O_3$	pH	$(NH_4)_2:B_2O_3$	pH	$(NH_4)_2O:B_2O_3$	pH	$K_2O:B_2O_3$	pH
20	1:4.15	7.15	1:3.06	8.27	..	..	1:2.36	9.17
30	1:3.92	7.03	1:2.96	8.18	..	..	1:2.42	8.96
40	1:3.57	7.02	..	..	1:2.88	8.05	1:2.42	8.86
60	1:3.27[a]	6.68	..	..	1:2.63[b]	7.97	..	..

[a] Sborgi (8).
[b] Sborgi and Ferri (9).

The suppression of boric oxide solubility in the mixed sodium-potassium system tends to disappear with rising temperature, although the pH relationships remain much the same. The solubility depression is still evident at 30° C. (first, third, and fifth experiments in Table II); but at 40° C. the mixed system has a higher boric oxide solubility than either alkali separately. This is due to a widening of the solubility peak for each individual alkali, so that the intermediate pH is no longer a region of particularly low solubility for each individual alkali system.

The effect of mixing all three alkalies is shown in the seventh experiment in Table I. Here excesses of sodium penta- and diborate, ammonium penta- and diborate, and potassium penta- and diborate were shaken with water at 20° C. These results are not easy to explain. The pH is high (9.05) and the potassium ion solubility approaches that of the peak potassium solution at pH 9.17. The ammonium content, however, is higher than in the mixed ammonium-potassium system, although the pH is further removed from the optimum pH for the ammonium system. Similarly, the sodium content is much the same as that of the mixed sodium-potassium system, although the pH is higher.

These anomalies do not appear in the results of experiments with combinations of all three alkalies at 30° and 40° C. At both these temperatures the pH of the combination is intermediate between the pH's of the individual alkalies, and between the pH's of the various pairs of alkalies. Moreover, the amount of each alkali dissolving in the combination appears to be controlled by the pH of the final solution.

The theory here advanced, that the amount of boric oxide dissolving at any one temperature is dependent mainly on the pH of the final solution, offers an explanation for many of the published figures on the solubility of boric acid in solutions of other salts (11). Thus a number of investigators have measured the solubility of boric acid in solutions of such compounds as inorganic acids, sodium chloride, sodium citrate, sodium acetate, and sodium potassium tartrate. A series of such solutions saturated with boric acid at 18° C. was made up following Kolthoff's figures as quoted by Seidell (11, p. 121) and the pH values were measured at 20° C.

Solvent	B_2O_3 Wt. %	pH
1.0M hydrochloric acid	2.07	0.09
Water	2.56	3.76
0.5M sodium sulfate	3.06	3.85
0.25M sodium oxalate	3.20	5.20
1.0M sodium acetate	3.79	5.80
0.5M sodium citrate	5.29	5.89

These figures suggest that the increase in boric oxide solubility is due to the rise in pH. The pentaborate formed by this increase in pH has its solubility suppressed to some extent by the presence of the common sodium ion of the solvent compound. Work is being continued on this effect of other compounds on the solubility of boric acid, to see how many of the known cases can be explained by this pH theory.

As for the formulation of solutions of maximum boric oxide solubility (the purpose of this investigation), the results show that at 20°, 30°, and 40° C. the peak boric oxide solubility of the simple sodium oxide-boric oxide system can be substantially increased by changing to the sodium oxide-ammonium oxide-boric oxide system. Moreover, in this latter system the composition limits of the solubility peak are no longer narrow, and by varying the sodium oxide-ammonium oxide ratio it is possible to vary the pH over more than 1 pH unit without greatly influencing the boric oxide solubility.

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Density, Electrical Conductance, and pH of Solutions in the System $CaO-P_2O_5-H_2O$ at 25° C.

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Information concerning the properties of phosphoric acid and calcium phosphate solutions is applicable to many problems in the phosphate industry, agronomy, and biochemistry. The density, electrical conductance, and pH of solutions in the system $CaO-P_2O_5-H_2O$, as measured by standard methods, are reported here. Compositions of the solutions were bounded by the line $P_2O_5-H_2O$ and the solubility isotherms of anhydrous dicalcium phosphate and monocalcium phosphate monohydrate (3, 6).

The electrical conductance of 0.001 to 18.02 molal solutions of phosphoric acid at 25° C. and the limiting conductance of the H_2PO_4 ion have been reported (14). Precise measurements of the density of solutions of phosphoric acid at 25° C. were reported recently (5).

PREPARATION OF SOLUTIONS

Water for preparing the solutions, purified in a conductance water still, had a maximum specific conductance of 2×10^{-6} ohm^{-1} cm.$^{-1}$. The phosphoric acid was purified by triple crystallization as either the anhydrous (17) or hemihydrate (15) form. The concentration of solutions prepared from these crystals was determined from the densities of the solutions (5). The two sources of acid