

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_5 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	5.49

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 $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ 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 $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$, as measured by standard methods, are reported here. Compositions of the solutions were bounded by the line $\text{P}_2\text{O}_5-\text{H}_2\text{O}$ 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 $2 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. 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

yielded solutions that in density, conductance, and pH were indistinguishable.

Monocalcium phosphate monohydrate was thrice crystallized from 50% phosphoric acid solution (12) and the crystals, washed with water-free acetone, had crystallographic and optical properties agreeing with those published (2, 12). A microscopic examination disclosed no extraneous phases, and a spectrographic analysis disclosed no significant amounts of impurities.

Solutions of known composition were prepared by mixing weighed amounts of monocalcium phosphate monohydrate, water, and phosphoric acid of known concentration. A series of such solutions, containing different amounts of the calcium salt, was prepared for each concentration of phosphoric acid, and stored in rubber-stoppered, borosilicate glass flasks. Weights were corrected to vacuum. The 1953 atomic weights (18) were used in calculations of molalities.

METHODS OF MEASUREMENT

Density. Density was measured in pycnometers fitted with ground-glass stoppers. This method has been described (4). The density of the standardizing liquid, conductance water at 25° C., was taken as 0.99707 gram/ml. The solutions were brought to thermal equilibrium in a water bath maintained at 25° ± 0.02° C. The weights were calibrated, and all weighings were corrected to vacuum.

Electrical Conductance. Electrical conductance was measured at 25° ± 0.001° C. with the equipment and methods used by Mason and Culvern (14). The results were corrected for calibration of the electrical bridge and for conductance of the water. The cells were standardized with solutions of potassium chloride (13) that had been thrice crystallized from water and fused.

The Beckmann thermometer for measuring the temperature of the oil bath was calibrated against a platinum resistance thermometer that had been calibrated by the National Bureau of Standards. The resistance thermometer was read with a calibrated Mueller resistance bridge.

pH. Measurements of pH were made at 25° ± 0.02° C. with a modified Hildebrand hydrogen electrode (11) and a Beckman No. 4970 calomel half-cell having a saturated potassium chloride bridge. The pH cell was a borosilicate glass H-cell just large enough to contain the electrodes and 5 ml. of the test solution. The potassium chloride in the salt bridge was purified by three recrystallizations.

The hydrogen electrode was made of a 0.5-mm. platinum wire that extended 2.5 cm. beyond its seal in the end of a 5-mm. borosilicate glass tube. Immediately before each use, the electrode was cleaned (1) and platinized in a chloroplatinic acid solution (7). To obtain the recommended current density, a current of 100 ma. was passed during platinization, and the current was maintained for periods ranging from 0 to 180 seconds, depending upon the test solution whose pH was to be measured. The platinized electrode was washed for 1 minute in a voluminous stream of tap water and then rinsed with the test solution.

Purified hydrogen (7) was washed in bubblers that were immersed in the bath containing the pH cell, once with water and twice with the test solution. The e.m.f. of the pH cell became constant within 0.1 mv. in 10 to 100 minutes. The time required for equilibration generally increased as the concentration of the test solution was increased.

The calomel half-cell was standardized against four National Bureau of Standards buffer solutions: 0.01-molar borax, 0.025-molar potassium dihydrogen phosphate-disodium hydrogen phosphate, 0.05-molar potassium acid phthalate, and 0.01-molar potassium hydrogen tartrate. A 0.1-molar hydrochloric acid solution, prepared from the constant-boiling mixture, was an additional standard. From the mean activity coefficient in water at 25° C. of hydrochloric acid (9) and of potassium chloride (8), and an assumption that the activity of the chloride ion in the re-

spective solutions is the same when the solutions have the same ionic strength, the pH of the 0.1-molar hydrochloric acid solution was calculated to be 1.085.

The E_{pH}° of the calomel half-cell at 25° C. was 0.2442 volt absolute. The pH values were calculated from the equation

$$\text{pH} = \frac{E - E_{\text{pH}}^{\circ}}{2.30259 \text{ RT/F}} = \frac{E - 0.2442}{0.059156}$$

where the values for R, T, and F are those published in 1952 (16); E is the measured e.m.f. in volts absolute; and E_{pH}° is treated as a constant (10).

RESULTS

To make the results readily usable, the observed values were used to derive a table giving secondary values for the properties at round values in molal concentrations of phosphoric acid and monocalcium phosphate. Interpolations were made on the assumption that, over small ranges of composition, the values of density, specific conductance, and pH are linear functions of composition. The interpolations were calculated by the equation

$$N_i = N + \frac{\partial N}{\partial m_A} \delta m_A + \frac{\partial N}{\partial m_S} \delta m_S$$

where N_i = interpolated value of density, specific conductance, or pH

N = measured value

m_A = molality of H_3PO_4

m_S = molality of $\text{Ca}(\text{H}_2\text{PO}_4)_2$

Most of the adjusted concentrations differed from the primary values by only a few thousandths of a molal unit. The adjustments in values of density, specific conductance, and pH, correspondingly small, were made with sufficient accuracy by taking the slopes, $\partial N / \partial m$, from large plots of the measured values against the molalities of the acid or of the salt. The values at round molalities are shown in Table I.

Tables giving values for the properties at round concentrations in weight per cent of phosphorous pentoxide and calcium oxide were derived from the data in Table I. The interpolated values of density in Table II, of specific conductance in Table III, and of pH in Table IV, were read from large-scale plots of the respective quantities against the per cent of phosphorus pentoxide. Each of these plots contained lines of constant per cent of calcium oxide.

From the deviations between the measured and interpolated quantities it was calculated that the probable error of the interpolated values of density and specific conductance is ± 0.0002, with a 99% confidence limit of ± 0.0005. The probable error of the interpolated pH values is ± 0.01, with a 99% confidence limit of ± 0.026.

Within the limits of concentration covered in this study, values for density and either specific conductance or pH are sufficient to define the composition of a solution in the system $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ at 25° C. The interpolated values are expected to be useful in the development and control of processes in which phosphoric acid and calcium phosphate solutions are involved.

The densities and specific conductances are fundamental physicochemical properties of the solutions. The significance and practical utility of pH values are reviewed elsewhere (10).

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