concentration cells with liquid junction containing barium chloride covering the range from 0.001 molal to 1.0 molal. These data when combined with Lucasse's data on concentration cells without liquid junction lead to the conclusion that

$$t = \frac{1.4450}{1 + 0.07135\sqrt{c}} - 1$$

Transference numbers computed by this formula agree with those obtained by the analytical method within 0.0024 over the entire range of concentration up to 1.0 molal.

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THE SYSTEMS: STRONTIUM OXIDE–PHOSPHORUS PENTOXIDE–WATER, AND BARIUM OXIDE–PHOSPHORUS PENTOXIDE–WATER AT 25° (ACID REGION)

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No investigation of the systems $SrO–P_2O_5–H_2O$ and $BaO–P_2O_5–H_2O$ has been reported in the literature. Investigation of the closely related system $CaO–P_2O_5–H_2O$ has been made by Cameron and his co-workers[2] and by Bassett.[3] Fairhall[4] has studied the system $PbO–P_2O_5–H_2O$.

Each system is one of three components. By working at a constant temperature, such a system may be made univariant, in which case the existence of a single solid phase is indicated by a variation in the composition of the solution. The formation of a second solid phase produces an invariant system, the solution being constant. Analyses of the solid and liquid phases of a series of empirical mixtures which have been permitted to attain equilibrium afford the data necessary for defining the conditions under which the different compounds exist in solid form.

For this investigation only those conditions under which at least three phases—gas, solid and solution—exist in equilibrium were of interest and the isotherms at 25° were determined. The composition of the solid phases was found by extrapolation, using Schreinemaker's[5] residue method. Analyses were made of the saturated solution and of the solid residue together with the adhering mother liquor. The values from the two analyses when plotted on a coördinate system lie on straight line, which when projected passes through a point representing the composition of

[1] DuPont Fellow at the University of Washington, 1926–1927.

[2] (a) Cameron and Seidell, THIS JOURNAL, **27**, 1503 (1905); (b) Cameron and Bell, *ibid.*, **27**, 1512 (1905).

[3] (a) Bassett, *Z. anorg. chem.*, **59**, 1 (1908); (b) *J. Chem. Soc.*, 111, 620 (1917).

[4] Fairhall, THIS JOURNAL, **46**, 1593 (1924).

[5] Schreinemaker, *Z. physik. Chem.*, 11, 81 (1893).

the solid phase. Similar lines located by the analyses of different mixtures at equilibrium pass through a common point which represents the composition of the solid phase.

Owing to the fact that phosphoric acid is very soluble, while strontium and barium oxides are only sparingly so, the entire range of experiments cannot be carried out easily in the same way; adsorption by the solid phase in alkaline solution is another complicating factor. The acid region only is treated in this paper. Further information regarding the compounds which exist in the basic region is given in the paper which follows.

Experimental Part

1. **Preparation of Materials.**—All of the materials used in the preparation of various salts were high grade "c. p. Analyzed" chemicals. The sirupy phosphoric acid (85%) gave negative tests for hydrochloric and sulfuric acids, heavy metals and reducing substances. The water used was the "conductivity water" of the laboratory, specific conductance approximately 2×10^{-6} mhos.

The monophosphates of strontium and barium were prepared by dissolving the hydroxides with an excess of moderately concentrated phosphoric acid, evaporating until crystals began to appear on the surface of the solution and then cooling rapidly with stirring to produce small crystals. The density of these solutions was so great that it was found advisable to use some means of stirring during their evaporation. The crystals were filtered by suction and washed with alcohol and then with ether. The alcohol and ether employed were anhydrous to prevent hydrolysis of the salts. The salts contained no water of hydration and analyses gave the following values: monostrontium phosphate, 36.60% SrO, 50.13% P_2O_5, ratio P_2O_5/SrO, 1.370 (theoretical, 1.371); monobarium phosphate, 46.69% BaO, 42.65% P_2O_5; ratio, P_2O_5/BaO, 0.933 (theoretical, 0.926).

Distrontium phosphate was made by adding slowly to a solution of 50 cc. of sirupy phosphoric acid per liter of water, solid powdered strontium hydroxide until a small amount remained undissolved, meanwhile keeping the solution rapidly stirred. The solid material was removed by filtration. The filtrate was next slowly heated and rapidly stirred. At about 60° a very fine precipitate of distrontium phosphate began to form, due to the hydrolysis of the monostrontium phosphate in solution. The precipitation was nearly complete when 75° was reached. The precipitate was filtered by suction and washed with alcohol and ether.

A different procedure was necessary for the preparation of dibarium phosphate. To a solution containing approximately 50 g. of barium oxide and 60 cc. of sirupy phosphoric acid per liter, dilute carbonate-free ammonium hydroxide (5%) was added drop by drop, the solution being thoroughly stirred. The gelatinous particles of tribarium phosphate which formed when the drops of ammonium hydroxide came in contact with the solution rapidly dissolved when stirred. The dibarium phosphate separated in crystalline form. The acidity of the solution at the end of the precipitate varied from *P*H 5 to 6.5.

2. **Methods of Analysis.**—(a) Strontium.—The sample was dissolved in 25 to 50 cc. of distilled water with the addition of 1 to 2 cc. of concentrated hydrochloric acid. Then an amount of alcohol exactly equal to the combined volume of aqueous solution and dilute sulfuric acid (1:20) used as the precipitating agent was added. Next, 5 to 10 cc. of the sulfuric acid solution was run in drop by drop while the solution was stirred. After standing from six hours to overnight at 10°, the precipitate of stron-

tium sulfate, which meanwhile became crystalline, was filtered in a Gooch crucible, washed with 50% alcohol and moderately ignited.

(b) Barium.—The determination of barium was made in the usual manner in the form of the sulfate.

(c) Phosphorus.—The phosphorus determination was made using the filtrate from the strontium and barium sulfate precipitations. The filtrates were boiled to expel alcohol and then evaporated to small volume. Often the filtrates were diluted to a given volume and an aliquot portion taken. The solution was made slightly acid, as shown by the indicator brom thymol blue. Then phosphorus was precipitated by the addition of magnesia mixture,[6] followed by slowly adding dilute ammonium hydroxide until the precipitate of magnesium ammonium phosphate had completely formed. After half an hour concentrated ammonium hydroxide was added to the extent of one-eighth the volume of the solution. After standing overnight the precipitate was separated by filtration and dissolved in hydrochloric acid. The phosphorus was then reprecipitated as magnesium ammonium phosphate, filtered and finally ignited to constant weight as magnesium pyrophosphate.

3. Experimental Procedure.—To aqueous solutions of phosphoric acid of varying concentration were added the solid phosphates, the solid mono- and diphosphates to saturation. This was done by adding one phosphate until the solution was almost saturated and then adding the other phosphate in small quantity; for example, if the monophosphate was first used a small quantity of the diphosphate was used to "seed" the solution. After "seeding," the bottles containing the solution were tightly stoppered and carefully sealed. The bottles were then placed either in an oven maintained at 35°, or placed directly in a thermostat maintained at 25 ± 0.03°. Final equilibrium was attained in all cases at the latter temperature.

Series A and C were made up with monostrontium phosphate, Series D with distrontium phosphate, Series E and F with monobarium phosphate and Series G with dibarium phosphate. Series C and E were kept at 35° for three weeks in order to saturate them at that temperature. The former (Series C) was then allowed to stand at 25° for five weeks with thrice daily shakings while the latter was shaken constantly for one week at the same temperature. None of the others was ever heated to a higher temperature, since they were more dilute in phosphoric acid and hydrolysis would probably occur at the higher temperatures. Series A, D, F and G were allowed to stand at 25° for three weeks with thrice daily shakings. A and F were then shaken constantly for two weeks and D and G for three weeks at this same temperature. At the end of the period of shaking the solid and liquid phases of all samples were analyzed.

To obtain the samples for analysis the bottle containing the desired solution was removed from the thermostat, quickly wiped dry, opened and about 25 cc. of the solution filtered by suction into a small vial. In order to prevent evaporation by drawing air through the moist residue, the suction was turned off just as all of the liquid had passed through the filter. The Gooch crucible used in this filtration had a thin layer of asbestos on the bottom to keep any small crystals from going through. On top of this was a Witt plate to protect the thin asbestos mat and on top of all was a small disk of hardened filter paper. The solid could be easily removed from the filter paper without tearing or damaging it in any way. In very concentrated phosphoric acid solutions the paper was not used.

The clear filtrate was used for the density determination and for the sample for the analysis of the liquid phase. During the filtration and density determination, the room temperature was maintained near 25°. The entire wet solid was analyzed. The

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[6] Employed the magnesia mixture recommended by Lundell and Hoffman, *J. Ind. Eng. Chem.*, 15, 44 (1923).

evaporation of water from either the liquid or solid phases was almost entirely prevented by placing the samples in tared, stoppered weighing bottles immediately after filtration. All the samples were then weighed within the following ten minutes.

Duplicate determinations on separate weighed portions of the solution were made in almost all cases, while a single determination on the solid phase was deemed sufficient; in many cases there was not sufficient material for duplicate determinations. The results are given in tabular form in Tables I and II, and graphically in Figs. 1 and 2.

TABLE I

ANALYSES OF LIQUID AND SOLID PHASES OF THE SYSTEM $SrO-P_2O_5-H_2O$

	Liquid phase		Solid phase		
Expt.	Strontium as SrO, %	Phosphorus as P_2O_5, %	Strontium as SrO, %	Phosphorus as P_2O_5, %	Density of liquid phase
CA	0.05	61.97	24.91	53.90	1.687
CB	0.13	56.49	25.67	52.01	1.594
CC	0.44	51.07	25.62	50.55	1.527
CE	1.78	43.80	27.36	48.55	1.455
CF	3.24	38.73	24.90	46.33	1.418
CG	4.61	35.90	26.48	45.68	1.410
CH	6.52	31.65	26.77	45.22	1.394
CI	8.08	27.63	27.82	43.54	1.379
AA	8.42	25.92	28.17	43.23	1.360
AB	8.88	24.71	28.46	42.72	1.357
AC	9.25	23.58	(a)	(a)	1.351
AD	7.84	20.79	35.02	30.80	1.294
AE	7.52	19.81	32.22	29.38	1.278
AF	6.53	16.66	32.27	28.18	1.230
AG	6.32	13.41	37.65	29.22	1.194
DA	5.11	12.70	(b)	(b)	1.169
AH	4.13	7.80	50.89	35.68	1.112
AI	3.18	6.02	45.11	32.05	1.083
DB	2.67	5.68	(b)	(b)	1.074

(a) Insufficient for analysis, microscopic examination showed it to be monostrontium phosphate. (b) Insufficient for analysis; microscopic examination showed it to be distrontium phosphate.

TABLE II

ANALYSES OF LIQUID AND SOLID PHASES OF THE SYSTEM $BaO-P_2O_5-H_2O$

	Liquid phase		Solid phase		
Expt.	Barium as BaO, %	Phosphorus as P_2O_5, %	Barium as BaO, %	Phosphorus as P_2O_5, %	Density of liquid phase
EB	0.85	53.79	38.43	43.28	1.580
EC	1.02	52.61	37.17	43.54	1.561
ED	1.50	49.22	37.17	42.69	1.524
EE	2.72	44.34	37.77	42.03	1.483
EG	6.93	33.74	39.26	40.65	1.425
FA	7.41	32.68	35.68	39.88	1.420
EH	9.14	28.36	37.09	38.81	1.397
EI	10.86	23.46	36.79	36.93	1.354
FB	8.50	16.15	51.46	26.70	1.246

Table II (*Concluded*)

	Liquid phase		Solid phase		
Expt.	Barium as BaO, %	Phosphorus as P_2O_5, %	Barium as BaO, %	Phosphorus as P_2O_5, %	Density of liquid phase
FC	6.84	12.35	Lost	Lost	1.188
GA	6.09	11.36	50.18	25.16	1.166
FD	6.31	11.19	59.46	28.82	1.165
FE	4.80	8.25	Lost	Lost	1.118
GB	4.33	7.61	37.90	20.08	1.107
FF	3.66	5.95	52.38	24.93	1.085
GC	2.00	2.96	37.44	18.49	1.040

Fig. 1, representing the system $SrO–P_2O_5–H_2O$, shows two stable phases, distrontium phosphate, Sr_2HPO_4, and monostrontium phosphate, $SrH_4(PO_4)_2$. The region in which the former is stable is bounded by A B C, and the latter by C D E. The area A C E represents the region which is not saturated and where no solid phase can be in equilibrium. Any region above the area A B C D E represents a state of supersaturation. At the point C, approximately, the two solid phases are in equilibrium with the solution. It is unfortunate that in experiment A C (Table I)

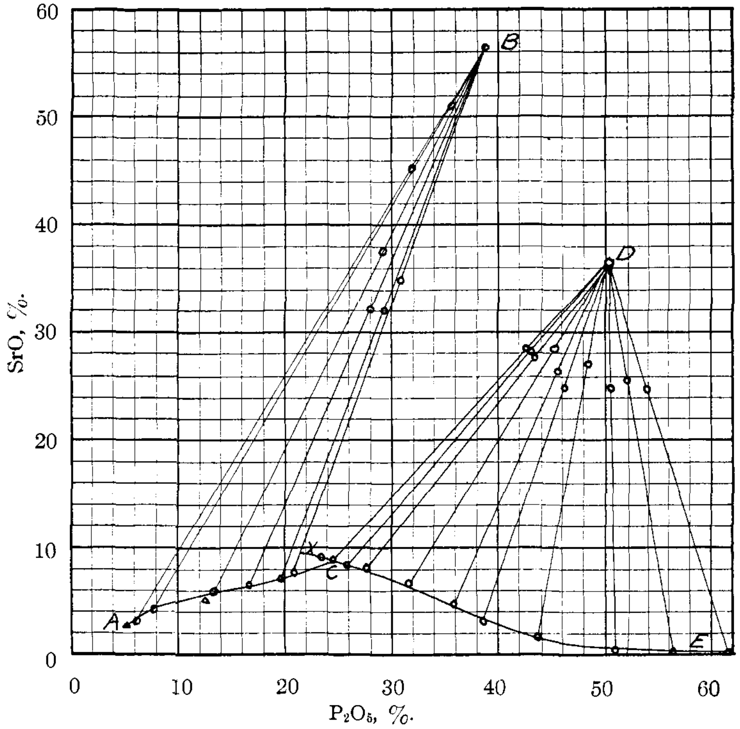

Fig. 1.—The system $SrO–P_2O_5–H_2O$.

the solid phase was too small for analysis; these data would show more conclusively the exact location of the invariant point. The extension C X probably represents a state of supersaturation with respect to distrontium phosphate as the solid phase. The lines A C and C E may be regarded as the solubility curves of di- and monostrontium phosphate, respectively, with respect to solutions of varying content of phosphoric anhydride.

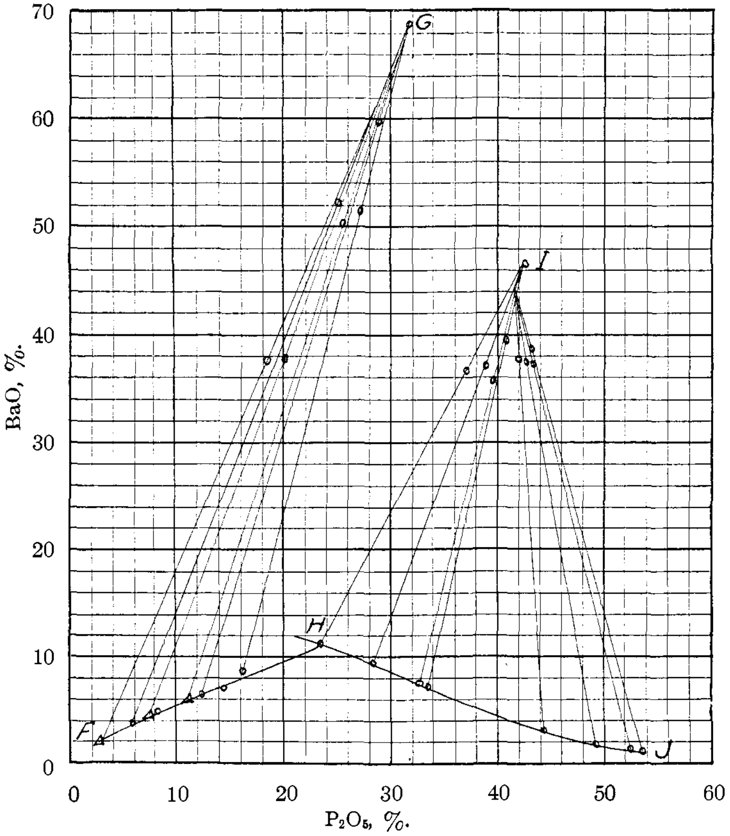

Fig. 2.—The system $BaO-P_2O_5-H_2O$.

The system $BaO-P_2O_5-H_2O$, represented in Fig. 2, is very similar to the $SrO-P_2O_5-H_2O$ system. Within the range of acidity of the system studied there are two stable solid phases. These are anhydrous di- and monobarium phosphates, represented by points B and I. The line FH represents the solution in stable equilibrium with dibarium phosphate and the line H J the stable equilibrium with monobarium phosphate. The point represented by H is the solution which can be in stable equilibrium with both di- and monobarium phosphates.

Summary

1. A phase rule study has been made of the system $SrO-P_2O_5-H_2O$ in the acid region. The limits at 25° have been defined for the two solid phases, monostrontium phosphate and distrontium phosphate.

2. A similar study has been made of the system $BaO-P_2O_5-H_2O$, in which the limits are defined for the solid phases, monobarium phosphate and dibarium phosphate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

A BASIC PHOSPHATE OF CALCIUM AND OF STRONTIUM AND THE ADSORPTION OF CALCIUM HYDROXIDE BY BASIC CALCIUM PHOSPHATE AND BY TRICALCIUM PHOSPHATE

BY JAMES R. LORAH,[1] HERMAN V. TARTAR AND LILLIAN WOOD[2]

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The purpose of this research was to clarify somewhat the confusion regarding the existence of phosphates of calcium more basic than the tertiary phosphate, $Ca_3(PO_4)_2$. To make the investigation more comprehensive the existence of basic phosphates of barium and of strontium was included.

Basic phosphates of calcium, strontium and barium have been mentioned frequently in the literature but apparently they have never been prepared in pure form.

Blarez[3] reported analyses of basic phosphates of calcium, strontium and barium which showed an excess varying from one-third to one-half molecule of the oxide over that required for the tertiary phosphates. Bertholet and Longuinine[4] had previously obtained similar results for barium phosphate.

Warington[5] found that when tricalcium phosphate is boiled with water the solution becomes distinctly acid. He made a series of experiments by boiling tricalcium phosphate with water for varying lengths of time, twenty-four to fifty hours, the water being renewed at frequent intervals. His analytical results do not show a final solid phase of constant composition; he concluded that the formula $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ "is the one which agrees best with the analyses." He further states, "We have, however, no certain ground for concluding that the action of boiling

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[1] DuPont Fellow at the University of Washington, 1926–1927.

[2] Miss Wood completed in 1920 a limited portion of the experimental work reported in this paper, *viz.*, Expts. 1a, 2a, 4a and 5a (Table I) in which the basic calcium phosphate was obtained.

[3] Blarez, *Compt. rend.*, 103, 264 (1886).

[4] Bertholet and Longuinine, *Ann. chim. phys.*, [5] 9, 33 (1876).

[5] Warington, *J. Chem. Soc.*, 19, 296 (1866); **26**, 983 (1873).