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

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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).

water finally results in the formation of such a hydrated oxygen apatite, since we do not know what the further prolonged action of boiling water might effect."

Cameron and Seidell[6] noted in the precipitation of tricalcium phosphate that "when the supernatant liquid was alkaline, however, the precipitate always contained a larger proportion of lime than is required by the formula for tricalcium phosphate." Cameron and Bell[7] prepared a series of mixtures by adding lime water or dicalcium phosphate to phosphoric acid, which were agitated for three months at 25°. They obtained a series of solid phases which gave ratios, P_2O_5/CaO, varying from that of dicalcium phosphate to one much below that secured by Warington. They postulated a series of solid solutions intermediate between dicalcium phosphate and calcium hydroxide.

The solid solution explanation of Cameron and his co-workers has been criticized by Bassett,[8] who performed a series of experiments in which he shook mixtures of calcium oxide, dicalcium phosphate and water for eighteen months at 25°. He points out the serious experimental difficulties involved and states, "There seems little doubt that in spite of the length of time allowed, equilibrium had not been maintained in many cases." In one range he obtained solid phases with ratios, P_2O_5/CaO, varying from 0.881 to 0.831, which approximate "to the 0.845 for tricalcium phosphate, and it seems legitimate to conclude that in the main these solids do actually consist of this compound." In another group he obtained solid phases with ratios ranging from 0.798 to 0.763 "which are not far removed from the 0.761 of oxyapatite $(Ca_3P_2O_8)_3 \cdot CaO$, of which they appear to consist." With an excess of calcium hydroxide Bassett reports a solid phase with a ratio as low as 0.549.

Kolthoff,[9] from his results on the titration of phosphoric acid with calcium hydroxide using phenolphthalein indicator, was of the opinion that he had obtained a quaternary compound.

Jolibois[10] claims that from certain mixtures of calcium hydroxide and phosphoric acid he quickly obtained a new crystalline phosphate, $P_2O_5 \cdot 2CaO–P_2O_5 \cdot 3CaO–10H_2O$. In a later paper Jolibois and Maze-Sencier[11] have shown that calcium hydroxide is very strongly adsorbed by tricalcium phosphate when the latter is precipitated in the presence of the former. Hayashi and Matsui[12] report that the amount of calcium hydroxide required for the complete precipitation of the phosphate ion

[6] Cameron and Seidell, THIS JOURNAL, **27**, 1503 (1905).

[7] Cameron and Bell, *ibid.*, **27**, 1512 (1905).

[8] Bassett, *J. Chem. Soc.*, **111**, 620 (1917).

[9] Kolthoff, *Chem. Weekblad*, **12**, 662 (1915).

[10] Jolibois, *Compt. rend.*, **169**, 1161 (1919).

[11] Jolibois and Maze-Sencier, *ibid.*, **181**, 36 (1925).

[12] Hayashi and Matsui, *J. Soc. Chem. Ind.* (*Japan*), **29**, 175 (1925).

from an alkaline sodium phosphate solution greatly exceeds the theoretical requirement for the formation of tricalcium phosphate.

Experimental Part

1. **Preparation of Materials.**—Tricalcium phosphate, $Ca_3(PO_4)_2$, was prepared from monocalcium phosphate, $CaH_4(PO_4)_2 \cdot H_2O$, which was produced in a manner precisely analogous to that given in the preceding paper for monostrontium phosphate. Twenty grams of the monocalcium phosphate was dissolved in four liters of water and then carbonate-free ammonium hydroxide was added with constant stirring until the solution was distinctly alkaline. The amorphous, gelatinous precipitate was washed with water by decantation, allowing several hours between washings for the precipitate to settle. The washing was continued until the phosphate-ion content of the water had decreased to a minimum. The small amount of phosphate ion in the wash water came from two sources: (1) the solubility of the tricalcium phosphate and (2) the slow hydrolysis of the tricalcium phosphate, which will be discussed later.

Tricalcium phosphate "has an inherent slowness of precipitation."[13] When sufficient ammonium hydroxide for complete precipitation was added at once, the solution was quite alkaline and a small amount of basic calcium phosphate was formed. Practically it was found desirable to add the ammonium hydroxide at such a rate that the solution never became more than faintly alkaline. Theoretically the hydrogen ion should not be allowed to decrease beyond the point at which the tricalcium and basic calcium phosphates are in equilibrium. Although this point is not definitely known, it is on the acid side of neutrality. Consequently, the tricalcium phosphate prepared by the method given above contained a small amount of basic calcium phosphate. Analysis of a dried sample gave the ratio P_2O_5/CaO, 0.835 (theoretical for tricalcium phosphate, 0.845).

Tristrontium phosphate was prepared by a method analogous to that employed for the preparation of tricalcium phosphate. A portion of the moist material was washed with alcohol, then with ether and dried at 80°. Analysis gave the ratio P_2O_5/SrO, 0.458 (theoretical 0.457) and showed 4.75% of moisture (calculated by difference).

A different procedure was required for the preparation of tribarium phosphate. When a moderate excess of ammonium hydroxide was added to a dilute solution of monobarium phosphate, the precipitate was a mixture of dibarium phosphate and tribarium phosphate, the former being present in much greater quantity. By adding drop by drop a very dilute solution of barium chloride to a boiling, dilute solution of sodium phosphate, Na_2HPO_4, which was made strongly alkaline with carbonate-free sodium hydroxide, a precipitate of tribarium phosphate was obtained. Analysis gave the ratio P_2O_5/BaO, 0.295 (theoretical, 0.309).

2. **Analytical Methods.**—Strontium and barium and most of the phosphorus determinations were made by the methods given in the preceding paper. A portion of the phosphorus determinations was made in the usual way; the sample was dissolved in nitric acid, the phosphorus precipitated with ammonium molybdate, this precipitate was dissolved

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[13] Holt, La Mer and Chown, *J. Biol. Chem.*, **64,** 509 (1925).

in ammonium hydroxide and the phosphorus precipitated twice as magnesium ammonium phosphate, ignited and weighed as the pyrophosphate.

Two methods were used for the estimation of calcium. A limited number of the determinations was made by precipitating with ammonium oxalate from a solution of the sample made slightly acid with acetic acid; then dilute ammonium hydroxide was added until the solution was only faintly acid, as shown by the indicator bromothymol blue. After standing hot for one hour the precipitate was filtered and titrated with standard potassium permanganate in the usual manner. This procedure is not quite as accurate as the usual one in which the precipitate is formed in ammoniacal solution; calcium oxalate is slightly more soluble in the acid solution.

The greater part of the calcium determinations was carried out by precipitating the calcium as sulfate. The sample was dissolved in 15 cc. of water, 2 cc. of concentrated hydrochloric acid and an amount of 95% alcohol equal to four times the volume of the aqueous solution were then added; finally, dilute (1:20) sulfuric acid was added drop by drop with constant stirring. After standing at 10° overnight, the calcium sulfate was filtered in a Gooch crucible, washed with 70% alcohol and gently ignited.

3. **Hydrolysis Experiments.**—A series of experiments was made treating the tertiary phosphates of calcium, strontium and barium with boiling water and with carbonate-free sodium hydroxide solution. A separate batch of phosphate was prepared for each experiment, which was carried out as follows. Approximately 10 g. of the moist phosphate which had not been dried was suspended in 4 liters of distilled water contained in a 5-liter Pyrex flask connected to a reflux condenser, the inner tube of which was also Pyrex glass. When hydroxide was present in the aqueous phase, the system was protected from the carbon dioxide of the air by a soda lime tube. The contents of the flask were boiled for eight hours each day. Every morning the supernatant liquid was carefully siphoned off and fresh water or solution added. At intervals a sample of the solid phase for analysis was removed with a pipet. The sample was washed with water and sometimes finally with alcohol and ether. The results of the hydrolysis experiments are reported in Table I.

All the samples were tested for the presence of carbonate with negative results.

The final product obtained from the hydrolysis of calcium phosphate gave a composition corresponding within experimental error to the compound $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$, for which the ratio P_2O_5/CaO is 0.760. The hydrolysis may be represented by the summary equation

$$10Ca_3(PO_4)_2 + 6H_2O = 3Ca_3(PO_4)_2 \cdot Ca(OH)_2 + 2H_3PO_4$$

The basic phosphate is very insoluble and the reaction proceeds to a definite hydrogen-ion concentration when equilibrium is reached. If

TABLE I

RESULTS FROM THE HYDROLYSES OF THE TERTIARY PHOSPHATES OF CALCIUM, STRONTIUM AND BARIUM

Expt.	Boiling period, days	P_2O_5/MeO	Liquid phase for hydrolysis
	Tricalcium Phosphate		
1a	0	0.835	......
	25	.763	Water
	46	.752	Water
2a	25	.752	Water
	46	.762	Water
4a	28	.763	Water
5a	26	.764	Water
1	36	.770	Water
4	27	.775	Water
5	28	.765	Water
7	28	.765	Water
8	27	.753	Water
8	60	.760	Water
21	8	.772	0.05 *M* NaOH
21	22	.761	0.05 *M* NaOH
3	9	.746	0.5 *M* NaOH

Expt.	Boiling period, days	P_2O_5/MeO	Liquid phase for hydrolysis
	Tristrontium Phosphate		
32	0	0.458	......
32	46	.439	Water
31	0	.458	......
31	8	.427	0.05 *M* NaOH
31	22	.422	0.05 *M* NaOH
31	45	.420	0.05 *M* NaOH
	Tribarium Phosphate		
11	0	.436	......
11	41	.422	Water
12	0	.329	0.05 *M* NaOH
12	20	.319	0.05 *M* NaOH

the acidic solution is removed by renewing the liquid in contact with the solid phase or by neutralizing the acid with alkali, the reaction proceeds to completion. After the solid phase reaches a composition giving the ratio P_2O_5/CaO, 0.76, it undergoes no change with further treatment.

The hydrolysis of the tristrontium phosphate took place more slowly than with the calcium salt. With water alone the conversion to the basic phosphate was very slow, only about half complete after forty-six days. In approximately half this time the material treated with dilute sodium hydroxide gave a solid phase corresponding in composition to the compound $3Sr_3(PO_4)_2 \cdot Sr(OH)_2$ (theoretical P_2O_5/CaO ratio, 0.411). No change occurred upon further treatment with the sodium hydroxide.

Tribarium phosphate was difficult to prepare and the samples used for the hydrolysis experiments contained considerable amounts of dibarium phosphate; approximately two-thirds of the sample treated with water and one-half of the sample treated with alkali. With water only the hydrolysis of the diphosphate was exceedingly slow; with sodium hydroxide it was slightly more rapid. Even after twenty days' treatment with the alkali the ratio P_2O_5/BaO was 0.319, indicating that not all of the material was converted to the tertiary phosphate.

4. Precipitation from Alkaline Phosphate Solutions.—A series of experiments was made to prepare basic phosphates of calcium, strontium and barium by precipitation in alkaline phosphate solutions.

Ten grams of purified calcium carbonate was dissolved in dilute hydrochloric acid and the solution evaporated to dryness to remove the excess of acid. The residue was taken up in 2 liters of water. This solution was slowly added from a pipet to a boiling solution of 23 g. of disodium phosphate (hydrate) and 95 cc. of saturated, carbonate-free sodium hydroxide solution in 2 liters of water. After standing overnight, the precipitate was washed with water until the wash water was practically free from chlorides. This required at least five washings with 3 liters of water each time, the solution being boiled for one hour to break up the large masses of precipitate, which was very gelatinous. Analysis of the dried precipitate gave the ratio P_2O_5/CaO, 0.781. Apparently the material was a mixture, largely the basic phosphate with some tricalcium phosphate.

The preparation of basic strontium phosphate was tried in a similar manner. A solution of 284 cc. of saturated strontium hydroxide (approximately 2.7 g. of $Sr(OH)_2$) was slowly added to a constantly stirred solution of 7.9 g. of disodium phosphate and 25 cc. of carbonate-free sodium hydroxide in 2 liters of boiling water. The flocculent precipitate was washed in the same manner as the calcium phosphate. Analysis gave the ratio, P_2O_5/SrO, 0.420, showing within experimental error that the material was the basic phosphate $3Sr_3(PO_4)_2 \cdot Sr(OH)_2$ (ratio, 0.411). The precipitate was then boiled for ten days longer with water (3 liters each day); after this treatment, analysis gave the ratio, P_2O_5/SrO, 0.423.

On adding drop by drop a very dilute solution of barium chloride to a dilute solution of disodium phosphate strongly alkaline with sodium hydroxide, a precipitate was obtained which gave the ratio, P_2O_5/BaO, 0.295, showing the material to be tribarium phosphate (theoretical ratio, 0.309). In all of the experiments no evidence has been secured of the existence of a basic barium phosphate.

5. Absorption Experiments.—In order to ascertain whether there is a reaction between the basic calcium phosphate reported above and calcium hydroxide or whether the basic substances often mentioned in the literature were materials produced by adsorption phenomena, some experiments were made on the adsorption of calcium hydroxide by the basic salt and by tricalcium phosphate. Two adsorption isotherms were determined for the basic salt, one after three days' and the other after six months' standing, and one isotherm for the tertiary phosphate after sixteen hours' standing.

(a) **With Basic Calcium Phosphate.**—Each experiment of the series was carried out in the following manner. The desired amount of recently boiled distilled water was placed in a dry, well-paraffined Pyrex bottle. To this was added two 25-cc. portions of a suspension of the basic calcium phosphate, the suspension being first thoroughly mixed by pouring from one flask to another. The use of a 25-cc. pipet twice, instead of a 50-cc. pipet once, reduced the error which might be due to any settling of the suspended material. The basic phosphate was prepared by the hydrolysis of tricalcium phosphate with water; ratio, P_2O_5/CaO, 0.765. The calcium hydroxide solution was then measured from a buret attached directly to the bottle, the system being carefully protected from the carbon dioxide of the air. The stopper of the bottle was then sealed carefully with paraffin. About 10 cc. of air space was left in the bottle so that the contents could be shaken. The bottle was then kept at 25 ± 0.03° and frequently shaken.

A blank was prepared in the same manner except that distilled water was substituted for the basic phosphate suspension.

The analysis of the basic phosphate suspension was made by determining the calcium and phosphorus in a weighed portion. From these data the weights of the basic calcium phosphate and of water in the suspension were calculated.

The concentration of the calcium hydroxide solution was determined by titration with carefully standardized hydrochloric acid with phenolphthalein indicator; the same acid was used for all the titrations. To determine the calcium hydroxide in the solution after adsorption, the bottle was allowed to stand for a day to allow the solid phase to settle. The seal was then broken and a 100-cc. portion of the solution rapidly removed and titrated. The blank was titrated in precisely the same manner. The data from the experiments with the basic phosphate are presented in Table II and in Figs. 1 and 2.

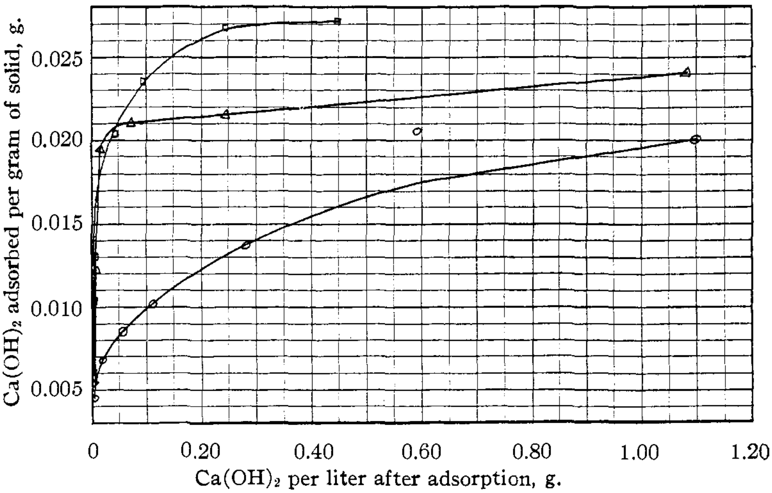
TABLE II

ADSORPTION OF CALCIUM HYDROXIDE BY BASIC CALCIUM PHOSPHATE AT 25°

0.8614 g. of basic calcium phosphate present in each bottle

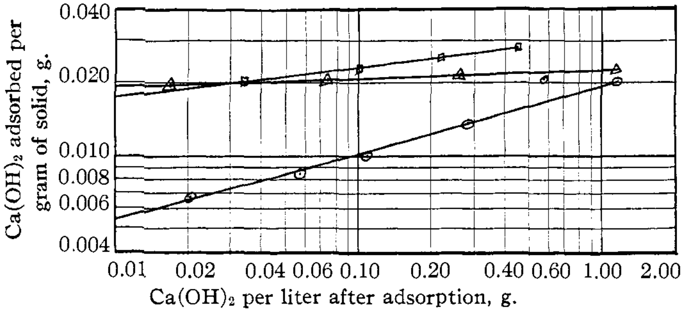
Bottle number	Init. concn. of $Ca(OH)_2$, g./l.	Final concn. of $Ca(OH)_2$, g./l.	Total vol. of soln., cc.	$Ca(OH)_2$ adsorbed per g. of solid, g.
		After Three Days' Standing		
25	1.176	1.099	224.69	0.0201
24	0.6706	0.5910	224.69	.0207
23	.3335	.2805	224.69	.0138
21	.1514	.1130	224.69	.0100
15	.0907	.0579	224.69	.0085
10	.0470	.0207	224.69	.0069
1	.0205	.0029	221.69	.0045
		After Six Months' Standing		
7	1.1760	1.0827	224.69	.0243
8	0.6706	0.5392	224.69	.0343
5	.3335	.2403	224.69	.0217
4	.1563	.0727	217.69	.0211
3	.0954	.0169	213.69	.0195
2	.0470	.0004	224.69	.0122
8	.0210	.0000	216.69	.0053

The curves from the two series of experiments (Fig. 1) are similar to the usual adsorption curve. When plotted logarithmically (Fig. 2), nearly straight lines are obtained, thus showing that the data may be represented by the common adsorption isotherm formulation proposed by Freundlich. There is no evidence of a reaction between basic calcium phosphate and calcium hydroxide. The two curves show that much more calcium hydroxide was taken up by the solid phase upon six months' standing. Usually adsorption equilibria are reached quickly and one might expect that if adsorption only took place there would be no further change after three days' contact. The change after this period may be due to the slow penetration of the calcium hydroxide into the interstices of the colloidal basic calcium phosphate. The writers are inclined to the opinion, however, that besides adsorption solid solutions were produced.



□, Tricalcium phosphate; △, six-month basic calcium phosphate; ○, three-day basic calcium phosphate.

Fig. 1.—Adsorption of calcium hydroxide by calcium hydroxide.



□, Tricalcium phosphate; △, six-month basic calcium phosphate; ○, three-day basic calcium phosphate.

Fig. 2.—Adsorption of calcium hydroxide by calcium phosphates.

The data confirm the varying ratios obtained by Bassett[8] and by Cameron and Bell,[7] and apparently corroborate for this region the solid solution explanation proposed by the latter investigators.

(b) With Tricalcium Phosphate.—The series of experiments with tricalcium phosphate was run in precisely the same manner as that with the basic phosphate except that the contact between the solid and calcium hydroxide was limited to sixteen hours to minimize the change due to the slow reaction between these substances to form the basic phosphate. The tricalcium phosphate was prepared in the manner previously described. The results are reported in Table III and in Figs. 1 and 2.

TABLE III

ADSORPTION OF CALCIUM HYDROXIDE BY TRICALCIUM PHOSPHATE AT 25° AFTER SIXTEEN HOURS

0.3838 g. of tricalcium phosphate present in each bottle

Bottle number	Init. concn. of $Ca(OH)_2$, g./l.	Final concn. of $Ca(OH)_2$, g./l.	Total volume of soln., cc.	$Ca(OH)_2$ adsorbed per g. of solid, g.
24	0.4990	0.4525	224.69	0.0272
23	.2848	.2388	224.69	.0269
15	.1390	.0989	212.69	.0234
10	.0699	.0348	224.69	.0205
1	.0278	.0043	224.69	.0131
47	.0188	.0011	224.69	.0103
48	.0110	.0002	224.69	.0064

The curves (Figs. 1 and 2) show that the data may be represented by the common adsorption isotherm formulation. The strong adsorption of calcium hydroxide by tricalcium phosphate affords at least a partial explanation of some of the basic materials which have been reported in the literature. Further experiments would be required to show whether solid solutions are possible in the range between tricalcium phosphate and the basic calcium phosphate.

Summary

1. The final product of the hydrolysis of tricalcium phosphate by water is a basic phosphate, the calcium and phosphorus contents of which correspond to that of the compound $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$. This compound is similar to the mineral apatite, the calcium fluoride or chloride of the latter being replaced by calcium hydroxide.
2. The point of equilibrium between tricalcium phosphate and basic calcium phosphate lies on the acid side of neutrality.
3. Tristrontium phosphate boiled with an aqueous solution of sodium hydroxide hydrolyzes to form a basic strontium phosphate, $3Sr_3(PO_4)_2 \cdot Sr(OH)_2$, analogous to the basic calcium phosphate.
4. The hydrolysis of tricalcium and of tristrontium phosphate proceeds more rapidly with a sodium hydroxide solution than with water.
5. The basic strontium phosphate may be prepared by direct precipitation from an alkaline phosphate solution.
6. A method has been given for the preparation of tribarium phosphate.

7. No evidence has been obtained to indicate the existence of a barium phosphate more basic than tribarium phosphate.

8. The isotherm for the adsorption of calcium hydroxide shows that in most concentrated solutions approximately one-third of a mol of calcium hydroxide was adsorbed per mol of basic phosphate. Comparison of the curves for the three days' and six months' period indicates that either the calcium hydroxide penetrates the interstices of the solid phase very slowly or solid solutions are formed.

9. The adsorption of calcium hydroxide by tricalcium phosphate is slightly greater than by the basic phosphate.

10. The strong adsorption of calcium hydroxide by tricalcium phosphate and by basic calcium phosphate affords a basis for an explanation of many statements in the literature regarding basic phosphates of calcium.

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THE EQUILIBRIUM IN AQUEOUS SOLUTION BETWEEN AMMONIUM ACETATE, ACETAMIDE AND WATER

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Introduction

The general reaction between ammonium salts of organic acids, the corresponding amides and water, though complicated by ionization and hydrolysis phenomena, in many instances runs smoothly and is adapted to studies in equilibria. In particular, it permits a comparison in equilibria among members of a homologous series.

E. E. Reid[1] has measured the benzamide formed upon heating until establishment of equilibrium of solutions of ammonium benzoate. Menschutkin[2] has studied the formation of amides on heating in closed glass tubes the pure ammonium salts of acids from formic to caproic, and also of benzoic and anisic acids. Other studies have been made purely from the standpoint of amide preparation.

E. A. Brodie, in this Laboratory, has measured the equilibrium between ammonium acetate and acetamide in aqueous solutions of several concentrations and at two temperatures. He heated the solutions to be brought to equilibrium in sealed pyrex glass tubes and analyzed the equilibrium mixtures through determination of their refractive indices. The present experiments are essentially repetitions of those of Brodie, substituting, however, for index of refraction, electrical conductance, thus lessening errors of analysis.

[1] Reid, *Am. Chem. J.*, **44**, 76 (1910).

[2] Menschutkin, *J. prakt. Chem.*, [2] **29**, 422, 436, (1884).