

Calcium Ammonium Orthophosphates

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Three new calcium orthophosphates— $\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and dimorphs of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ —were detected in experimental fertilizers and as products of reactions of fertilizers with soils. The crystallographic properties of the new salts were determined, and their fields of stability were defined in an exploration of the system $\text{CaO}-\text{NH}_3-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$ that covered the pH range 4 to 10. The results help to explain the reactions that occur in the ammoniation of superphosphate. When diammonium phosphate is the ammoniating agent, formation of apatite is avoided. Dicalcium phosphate and diammonium phosphate are not a stable salt pair; fertilizers containing these salts will cake by formation of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.

THREE new crystalline calcium ammonium orthophosphates were found in ammoniated superphosphates, suspension-type fertilizers, and products of the reactions of fertilizers with soils (7). The crystallographic properties of these salts were determined, and a brief study was made of their four-component system to define the conditions of stability of each salt.

The system calcium oxide-ammonia-orthophosphoric acid-water has not been studied thoroughly. Flatt *et al.* (2) examined the acidic region of this system and reported a salt with the composition $\text{Ca}_2\text{NH}_4\text{H}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$; Brown *et al.* (7) described the chemical and physical properties of this salt. Lasne (5) examined the highly basic region of the system and reported the salt $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$; the existence of this salt was confirmed in this laboratory.

The three new calcium ammonium orthophosphates— $\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and dimorphs of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ —exist in the region of the four-component system in which the pH ranges from 4 to 10. This region is of particular

interest in soil and fertilizer studies; it embraces also dicalcium phosphate dihydrate and hydroxyapatite as stable solid phases.

The results of the chemical and crystallographic examinations will be useful in identification of the new salts. Results of the phase-diagram study suggest methods for the preparation of ammoniated calcium phosphate fertilizers and may help to clarify some of the reactions of fertilizers with soil (7).

Preparation and Characterization

The calcium ammonium orthophosphates were prepared by adding calcium hydroxide or carbonate to concentrated ammonium phosphate solutions that had mole ratios of N:P in the range 1.0 to 3.4, and pH's in the range 4.0 to 9.9. The mixtures were filtered with suction, and the solid products were washed sparingly several times with dilute ammonium hydroxide, rinsed with acetone, and air dried.

Characterizations were limited to

products shown by petrographic and x-ray examination to be homogeneous and well crystallized. Chemical analyses were made on air-dried samples to avoid possible dehydration and loss of ammonia by drying at higher temperatures. The water contents, which were determined by difference, thus are slightly high. Phosphorus was determined spectrophotometrically (3), calcium gravimetrically (10), and ammonia by distillation with sodium hydroxide. The compositions of typical preparations of the salts are shown in Table I.

Dimorph B of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was first isolated by Lindsay *et al.* (8); they reported the composition $\text{Ca}_2(\text{NH}_4)_2(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$ from an analysis of one preparation that was recovered from an extract of a fertilized soil. The composition reported here is based on analyses of 10 homogeneous preparations that were precipitated under several different conditions.

The two forms of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ are readily distinguished by their optical and morphological properties, x-ray diffraction spectra, and solubility

Table I. Calcium Ammonium Orthophosphates

Compound	Composition, %							Moles per Mole P_2O_5			Moles per Mole P		
	Ca	CaO	N	NH_3	P	P_2O_5	H_2O (diff.)	CaO	NH_3	H_2O	Ca	N	H_2O
$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ Dimorph A	14.7	20.6	9.2	11.2	21.3	48.7	19.5	1.07	1.92	3.16	2.14	3.83	6.31
	14.9	20.8	9.3	11.3	21.3	48.8	19.1	1.08	1.94	3.08	2.16	3.86	6.16
Dimorph B	14.2	19.9	9.2	11.2	21.4	49.1	19.8	1.02	1.91	3.18	2.04	3.86	6.35
	13.5	18.9	10.0	12.1	21.7	49.7	19.3	0.96	2.04	3.06	1.92	4.06	6.12
Stoichiometric	14.01	19.60	9.79	11.90	21.65	49.61	18.89	1.00	2.00	3.00	2.00	4.00	6.00
$\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$	22.7	31.7	8.2	10.0	18.2	41.8	16.5	1.92	2.00	3.11	3.84	3.99	6.22
	23.4	32.7	7.8	9.5	17.9	41.1	16.7	2.01	1.93	3.20	4.03	3.85	6.40
Stoichiometric	23.42	32.77	8.19	9.95	18.10	41.48	15.80	2.00	2.00	3.00	4.00	4.00	6.00

Table II. Morphological and Optical Properties

Property	CaNH ₄ PO ₄ ·H ₂ O	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	
		Dimorph A	Dimorph B
Symmetry	Orthorhombic, class mmm	Monoclinic, class 2/m	Monoclinic, class 2
Habit	Thin plates tabular on N _y - N _z	Stout rods elongate on c; prominent {110}	Rods elongate on b; hemimorphic form
Refractive index			
N _α	1.588	1.521	1.506
N _β	1.590	1.542	1.510 ^a
N _γ	1.596	1.551	1.511
Optic sign	Biaxial (+)	Biaxial (-)	Biaxial (-)
Angle 2V			
Observed	...	65°	45°
Calculated	61°	66°	53°
Orientation	N _x (Bxo) ⊥ to tabular plane	N _x (Bxa) = b; N _y inclined to c by 25° in acute β on (010); β = 112°	N _z (Bxo) = b; N _y inclined to c on (010) by 18° in obtuse β; β' = 108°
Specific gravity			
Pycnometric	2.25	2.05	1.91
Calculated ^a	2.23	2.00	1.86

^a Computed from composition and refractive indices by the Gladstone-Dale relationship (4).

Table IV. Equilibrium in the System CaO-NH₃-H₃PO₄-H₂O at Room Temperature

Liquid Phase								Solid Phase ^a
Composition, %								
N	P	Ca	NH ₃	H ₃ PO ₄	CaO	pH		
6.7	9.8	...	8.1	31.3	A	
7.4	11.4	0.09	9.0	36.0	0.12	5.30	A	
10.5	14.6	0.02	12.7	46.2	0.03	6.00	A	
6.0	8.0	...	7.3	25.2	A + B	
9.2	11.4	...	11.2	36.2	...	6.41	A + B	
4.5	6.0	...	5.5	18.9	A + CaHPO ₄ ·2H ₂ O	
3.0	3.5	...	3.7	11.2	B	
4.6	5.7	...	5.6	18.1	B	
9.3	9.8	0.03	11.3	30.9	0.04	7.91	B	
1.8	2.3	...	2.2	7.2	CaHPO ₄ ·2H ₂ O	
3.0	3.8	...	3.7	12.1	CaHPO ₄ ·2H ₂ O	
3.8	8.1	...	4.6	25.7	...	4.02	CaHPO ₄ ·2H ₂ O	
6.4	10.3	0.07	7.7	32.7	0.10	5.12	CaHPO ₄ ·2H ₂ O	
0.9	0.8	...	1.1	2.4	CaNH ₄ PO ₄ ·H ₂ O	
3.8	2.1	0.002	4.6	6.6	0.003	9.89	CaNH ₄ PO ₄ ·H ₂ O	
4.6	4.6	...	5.6	14.6	CaNH ₄ PO ₄ ·H ₂ O	
4.7	3.7	...	5.7	11.8	...	9.43	CaNH ₄ PO ₄ ·H ₂ O	
9.1	9.2	...	11.1	29.1	...	8.28	CaNH ₄ PO ₄ ·H ₂ O	
3.0	3.0	...	3.6	9.5	CaNH ₄ PO ₄ ·H ₂ O + Ca ₅ (PO ₄) ₃ OH	
8.8	9.1	...	10.7	28.8	...	8.08	CaNH ₄ PO ₄ ·H ₂ O + Ca ₅ (PO ₄) ₃ OH	
0.8	0.8	...	1.0	2.5	Ca ₅ (PO ₄) ₃ OH	
1.8	2.1	...	2.2	6.8	Ca ₅ (PO ₄) ₃ OH	
4.4	4.8	...	5.4	15.1	Ca ₅ (PO ₄) ₃ OH	
5.9	6.1	...	7.2	19.2	Ca ₅ (PO ₄) ₃ OH	
6.2	6.5	...	7.5	20.6	Ca ₅ (PO ₄) ₃ OH	

^a A = dimorph A of Ca(NH₄)₂(HPO₄)₂·H₂O; B = dimorph B

characteristics. The morphological and optical properties of the three new calcium ammonium orthophosphates are listed in Table II, their x-ray diffraction patterns in Table III.

Equilibration Studies

Equilibration mixtures were prepared by adding calcium carbonate (0.25 to 1.0 gram) to saturated ammonium phosphate solutions (100 ml.). Most of the calcium was precipitated [maximum

Ca content was 0.09% (CaO, 0.12%)], but the compositions of the liquid phases were changed only slightly. The compositions of the most concentrated liquid phases were close to those of saturated solutions in the system ammonia-orthophosphoric acid-water at 25° C. described by Lenfesty and Brosheer (6); the diagram of the three-component system at 25° C. is the basis for the plot of the results in Figure 1.

Many of the equilibration mixtures were diluted with water to explore the

Table III. Powder X-Ray Diffraction Patterns of Calcium Ammonium Orthophosphates

(Cu K_α radiation; intensities read from goniometer tracings)

Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O					
CaNH ₄ PO ₄ ·H ₂ O		Dimorph A		Dimorph B	
d	I/I ₁	d	I/I ₁	d	I/I ₁
10.52	3	8.58	49	10.39	44
7.82	100	8.18	6	6.96	100
4.55	41	6.32	16	5.27	18
4.15	2	5.01	16	5.09	10
3.80	5	4.79	13	4.74	66
3.66	9	4.29	100	4.00	34
3.07	15	4.09	5	3.69	98
2.85	44	3.97	2	3.66	32
2.79	15	3.78	3	3.50	13
2.75	5	3.69	11	3.22	15
2.72	9	3.42	2	3.18	65
2.60	15	3.28	30	3.08	11
2.47	5	3.16	7	3.04	23
2.41	13	3.10	27	2.91	5
2.39	5	2.87	7	2.73	14
2.32	6	2.84	7	2.44	13
2.20	12	2.73	12	2.42	11
2.16	2	2.55	3	2.37	13
2.08	12	2.50	4	2.33	6
2.06	4	2.47	15	2.30	6
1.95	5	2.39	12	2.19	21
1.92	6	2.36	3	2.13	15
1.84	6	2.29	5	2.09	15
1.81	4	2.27	5	2.06	3
		2.20	2	2.03	13
		2.11	9	2.00	4
		2.05	2	1.98	4
		1.98	13	1.96	6
		1.88	13	1.89	5
				1.86	4
				1.83	11

region between the saturated solutions and the water corner. Each mixture was placed in a stoppered flask and allowed to stand, with daily shaking, at room temperature (25° to 27° C.).

Compositions of the concentrated liquid phases were determined by the analytical methods used on the solid preparations, and compositions of the liquid phases of the diluted mixtures were calculated from the amounts of saturated solution and diluent water. The pH was measured with a glass electrode and a portable pH meter. The course of each equilibration was determined by periodic petrographic examinations of the solid phase. Results obtained with about 100 equilibration mixtures are summarized in Table IV and Figure 1.

The regions in Figure 1 are projections on the three-component system of compositions of solutions in which hydroxyapatite, dicalcium phosphate dihydrate, and the three calcium ammonium orthophosphates are stable solid phases. The region in which CaNH₄PO₄·7H₂O appears (above pH 10) was not investigated.

Of the solid phases studied, hydroxyapatite precipitated most rapidly. Equilibrium with CaNH₄PO₄·H₂O, dicalcium phosphate dihydrate, or dimorph B of Ca(NH₄)₂(HPO₄)₂·H₂O

usually was attained within a day, whereas dimorph A of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ required a few days to several months for equilibration. In the region of dimorph A, dimorph B usually was formed rapidly as the initial precipitate, after which it disappeared slowly as dimorph A was formed. The boundary between the regions of these two phases in Figure 1 represents an apparently steady state after 5 months and probably is close to the equilibrium position.

Equilibration of mixtures in the region of dimorph A was completed within a few minutes by warming to 60°C ., but equilibration of mixtures in the region of dimorph B was not affected significantly by warming. Mixtures that were warmed to accelerate equilibration were then allowed to stand at room temperature and were examined periodically.

When mixtures containing dimorph A were diluted, alteration of the solid phase to dimorph B or dicalcium phosphate at room temperature required several weeks. Because of its low solubility, hydroxyapatite did not alter significantly when the composition of the mixture was changed to one in which apatite was not the stable solid phase. The other solids ($\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, dicalcium phosphate, and dimorph B) altered rapidly to the new stable solid phase when the composition of the mixture was changed.

Discussion of Results

The results of the equilibration studies are useful in interpretations of the reactions that occur in the ammoniation of calcium phosphate fertilizers. In the usual ammoniation of superphosphate, which is crude monocalcium phosphate, the ammonia is added either as a gas or as an aqueous solution. The composition of the ammonia source then lies on the ordinate of Figure 1, and the composition of the superphosphate can be projected on the abscissa. The composition of the mixture then lies on a line whose projection on the three-component diagram has a negative slope and cuts across the field of hydroxyapatite. In the usual ammoniation, ammonia is added to monocalcium phosphate, so that the projection of the total composition moves from the abscissa upward and to the left.

In the initial moment of ammoniation, particularly with a relatively dry superphosphate, the composition of the liquid phase moves rapidly from the ordinate across the apatite field, so that some apatite is unavoidable. As ammoniation continues, however, most of the reaction occurs in regions in which dicalcium phosphate is precipitated. Results of engineering studies (9) show that the composition of the product, in terms of

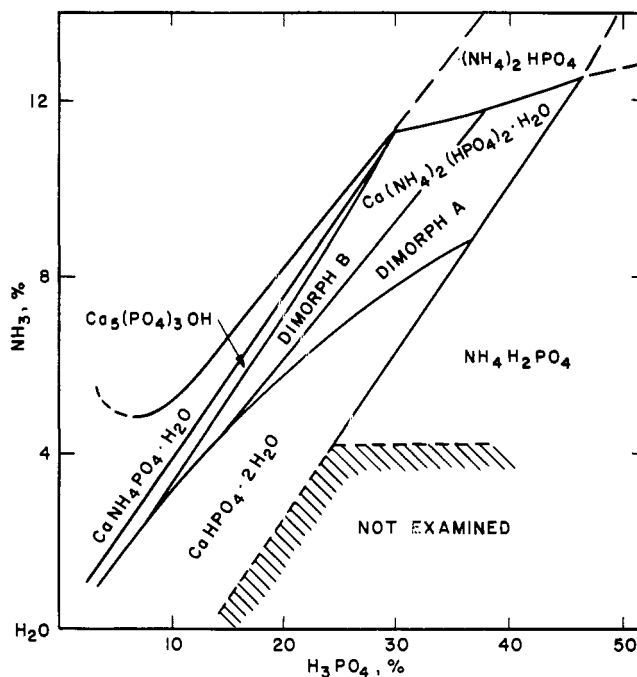


Figure 1. Regions of solid phases in the system $\text{CaO}-\text{NH}_3-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$
(Projected on the system $\text{NH}_3-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$)

the amount of apatite formed, is affected by the rate of addition of ammonia, temperature, moisture content, and porosity and particle size of the monocalcium phosphate. Care must be taken to prevent overammoniation in localized spots which shifts the composition of the solution into the apatite field. Apatite once formed alters very slowly to the more available compound with which the final liquid phase is in equilibrium.

The results show, however, that superphosphate can be ammoniated with diammonium phosphate without approaching the apatite field. Examination under the microscope of a mixture of diammonium phosphate and superphosphate showed that moisture condensed on the diammonium phosphate to form a concentrated solution that reacted with the superphosphate to form one or both of the dimorphs of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. As the solution became diluted by the precipitation reactions, the initial solid phases altered slowly to a mixture of dicalcium phosphate and monoammonium phosphate. As indicated in Figure 1, the solution formed initially lies along the diammonium phosphate isotherm, and its position depends upon the amount of monocalcium phosphate that dissolves. The initial composition, moisture content, and kinetic factors determine which dimorph of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is formed initially, but dimorph B usually is the initial phase. No apatite was observed in any of these tests.

Similarly, mixtures of diammonium

phosphate and gypsum were observed to form dimorph A of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, which then altered slowly to dicalcium phosphate dihydrate. The same reaction has been observed in the soil and explains why additions of gypsum decrease the salt injury to seedlings by diammonium phosphate.

The diagram of Figure 1 may be used as a guide in the preparation of slurry-type or suspension fertilizers without formation of apatite. Dimorph B of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is readily precipitated as a voluminous mass of needle crystals that behaves like a stable gel, and stable suspensions containing 5 to 9% nitrogen and about 17% phosphoric oxide can be prepared.

Figure 1 shows that diammonium phosphate and dicalcium phosphate dihydrate do not form a stable salt pair. Dry-mixed fertilizers containing these two salts probably will cake as a result of the formation of the dimorphs of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.

Both crystalline dimorphs of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ have properties desirable in a fertilizer. Their composition is about that of an ammoniated triple superphosphate that contains 4 pounds of nitrogen per unit of P_2O_5 , but, unlike the ammoniated superphosphate, the new salts release both their nitrogen and phosphorus into the soil slowly from a single source. The two dimorphs differ significantly in rate of solution, and their mixtures might be used as sources with controlled rates of release of nutrients. Greenhouse tests of these dimorphs are under way.

Literature Cited

- (1) Brown, W. E., Smith, J. P., Lehr, J. R., Frazier, A. W., *J. Phys. Chem.* **62**, 625 (1958).
- (2) Flatt, R., Brunisholz, G., Chapuis-Gottreux, S., *Helv. Chim. Acta* **34**, 884 (1951).
- (3) Gee, A., Deitz, V. R., *Anal. Chem.* **25**, 1320 (1953).
- (4) Larsen, E. S., Berman, H., *U. S. Geol. Surv. Bull.* **848** (1943).
- (5) Lasne, H., in "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," J. W. Mellor, ed., Vol. **III**, p. 878, Longmans, Green, London, 1928.
- (6) Lenfesty, F. A., Brosheer, J. C., *J. Chem. Eng. Data* **5**, 152 (1960).
- (7) Lindsay, W. L., Frazier, A. W., Stephenson, H. F., *Soil Sci. Soc. Am. Proc.* **26**, 446 (1962).
- (8) Lindsay, W. L., Taylor, A. W., *Trans. Intern. Congr. Soil Sci.* **7th**, Madison, Wis., 1960, Vol. **III**, pp. 580-9.
- (9) Sauchelli, V., "Chemistry and Technology of Fertilizers," p. 410, Reinhold, New York, 1960.
- (10) Willard, H. H., Boldyreff, A. W., *J. Am. Chem. Soc.* **52**, 1888 (1930).

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FERTILIZER MATERIALS

Vitreous Calcium Metaphosphate—Some Properties of Its Aqueous Systems

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In water, vitreous calcium metaphosphate forms a coacervate, a viscous solution of highly condensed phosphates, which hydrolyzes slowly to pyrophosphate. Incorporated silica decreases the formation of the coacervate and increases the solubility of the metaphosphate; incorporated alumina has the opposite effect. Vitreous calcium metaphosphate behaves in moist soil much as it does in water, and yields residues of calcium pyrophosphates.

THE PRODUCT of the dehydration and fusion of monocalcium phosphate monohydrate or of the reaction of phosphate rock with phosphoric oxide vapor at 1100° C. has a composition close to that of $\text{Ca}(\text{PO}_3)_2$. When cooled slowly from its melt, it crystallizes as β -calcium metaphosphate, which is quite insoluble and of little value as a fertilizer. When cooled rapidly from its melt, however, it solidifies as a glass that dissolves slowly in water and has considerable value as a fertilizer (δ) and as an intermediate in the preparation of other fertilizers. Little is known of the condensed phosphate species of which the vitreous material is composed, but for convenience it is referred to as calcium metaphosphate.

As part of a broader study of the behavior of vitreous calcium metaphosphate in the soil and in its processing into other phosphate fertilizers, a study was made of the calcium metaphosphate-water system. In water, vitreous calcium metaphosphate forms a water-immiscible coacervate and a dilute solution; the coacervate, the solution, and their degradation products were examined chemically, chromatographically, petrographically, and by x-ray powder diffraction. A study was made also of the effect of incorporated silica and alumina on the dissolution of the metaphosphate.

Materials and Procedure

Vitreous calcium metaphosphate was prepared by heating reagent grade monocalcium phosphate monohydrate in a platinum dish to fusion at about 1100° C. and quenching the melt. The products appeared to be clear glasses, but petrographic examination showed that they sometimes contained very small amounts of crystalline β -calcium metaphosphate. The mole ratio P:Ca (P_2O_5 :CaO) ranged from 1.980 to 2.044 (0.990 to 1.022), and the sum of the calcium and phosphorus contents ranged from 51.43 to 51.54% (CaO + P_2O_5 , 99.83 to 100.04%).

Vitreous metaphosphates containing dissolved silica or alumina were prepared by fusing and quenching mixtures of pure vitreous calcium metaphosphate and the oxide.

The fertilizer grade metaphosphate was a product of the TVA demonstration plant in which rock phosphate is treated with phosphoric oxide vapor at 1100° C. It contained Ca 19.0, P 27.4, Al 0.6, Fe 1.0, and Si 2.9% (CaO 26.6, P_2O_5 62.8, Al_2O_3 1.1, Fe_2O_3 1.4, and SiO_2 6.2%), and its mole ratio P:Ca (P_2O_5 :CaO) was 1.866 (0.933). Much of the silica in this material was present as unreacted quartz; the product usually contained 1 to 2% of β -calcium pyrophosphate.

In water, pure vitreous calcium metaphosphate yields a viscous, water-immiscible liquid (coacervate) and a dilute aqueous phase. The reaction is slow at room temperature; raising the temperature accelerates both the dissolution and the hydrolysis of the dissolved phosphate. The mole ratio P:Ca in both the coacervate and the dilute phase is the same as that in the original metaphosphate.

The coacervate may be prepared by covering crushed vitreous calcium metaphosphate with water and allowing the mixture to stand at room temperature with occasional stirring for about 3 days. The lighter aqueous phase is decanted off, and the coacervate is removed by pressure filtration. From an initial mixture of 85 grams of -60-mesh metaphosphate and 110 grams of water there was obtained 50 ml. (78 grams) of coacervate that contained 52% solute phosphate, which is defined for convenience as the sum of the calcium oxide and phosphoric oxide contents.

More conveniently, the apparatus in Figure 1 is filled with water to the level of the overflow and -20- plus 35-mesh metaphosphate is placed on a thin layer of glass wool on the perforated plate. Warm water is circulated through the jacket to maintain the temperature at 45° C., and water is dripped slowly onto the charge. The coacervate drips