

monocalcium phosphate may initially release solutions with pH's below 2 that contain appreciable amounts of calcium.

Potassium syngenite, which is relatively insoluble in water, might be expected to act as a slowly soluble source of potash. Results of exploratory

greenhouse tests, however, show little indication of this effect.

Literature Cited

- (1) Ando, J., Smith, J. P., Siegel, M. R., Jordan, J. E., TVA manuscript in preparation.

- (2) Taylor, A. W., Gurney, E. L., *J. Agr. Food Chem.* **13**, 92 (1965).
 (3) Wright, B., Lancaster, J. D., Anthony, J. L., Mississippi State Univ. Agr. Expt. Sta., *Tech. Bull.* **52** (1963).

Received for review March 18, 1964. Accepted June 5, 1964.

FERTILIZER TECHNOLOGY

Heat of Ammoniation of Superphosphoric Acid

EDWARD P. EGAN, Jr., and
 ZACHARY T. WAKEFIELD

Division of Chemical Development,
 Tennessee Valley Authority,
 Wilson Dam, Ala.

In the temperature range 100° to 200° C. the amount of ammonia absorbed by superphosphoric acid (33% P, 76% P₂O₅) rapidly enough to give a measurable heat effect increased with rising temperature. The heat of ammoniation of superphosphoric acid was measured at base temperatures of 100°, 125°, and 180° C.; the respective maximum ammonia concentrations were 1.24, 3.54, and 4.37 pounds of NH₃ per 20 pounds of P₂O₅, and the integral heats of ammoniation at the respective maximum ammonia concentrations were 3548, 3023, and 2862 B.t.u. per pound of NH₃. Ammoniation made only slight changes in the distribution of the phosphate species.

AMMONIUM polyphosphate, a mixture of the ammonium salts of ortho- and condensed phosphoric acids, is a new and promising fertilizer material (2, 7), prepared by ammoniation in a closed vessel at about 200° C. of superphosphoric acid that contains about 33% P (76% P₂O₅). Knowledge of the heat of ammoniation of superphosphoric acid is useful in plant design calculations.

Apparatus

The calorimeter was built around a stainless steel 300-ml. Parr oxygen bomb, fitted with a single gas port and a stainless steel stirrer driven at 590 r.p.m. A 100-ohm electrical calibrating heater was wound in a spiral groove in the outer surface of the bomb. The bomb was immersed in a bath of molten wax for measurements at 100° and 125° C. and of silicone oil for measurements at 180° C., the highest practicable base temperature for the assembly.

The liquid bath was contained in a stainless steel vacuum flask and was stirred by a stream of nitrogen from a sparger ring. The flask was fitted with a Transite lid that supported three stainless steel radiation shields. An electrical heater was wound on the outer surface of the vacuum flask, and the assembly was placed in an electrically heated oven that was maintained at a temperature suitably lower than that at which a run was made. The vacuum flask was pumped continuously.

The ammonia was admitted as a gas from a 300-cc. liquid ammonia tank through a 1/8-inch stainless steel tempering coil that passed through the oven and was attached to the top of the bomb. The pressure in the system was measured at the valve on the ammonia tank.

A precision temperature controller actuated by a resistance thermometer maintained the outer surface of the vacuum flask at the base temperature of each run. Each run was started with the calorimeter (bomb and liquid bath) within 0.1° C. of the base temperature. Calorimeter temperatures during a run were measured at 1-minute intervals with a calibrated platinum resistance thermometer in a glass case in the liquid bath. Straight-line cooling curves had slopes of 0.006° per minute at 180° C. and 0.054° per minute at 197° C.; the calorimeter thus was suitable for obtaining data of the reliability required for design calculations.

Reagents

The liquid ammonia from a synthesis plant was used as received.

Three samples of superphosphoric acid were used. The acid used for runs at 100° C. was not heat-treated sufficiently

to equilibrate the phosphate species (4, 5).

The acid for runs at 125° C. was a product of a demonstration-scale superphosphoric acid plant, and that for runs at 180° C. was made by adding reagent grade phosphoric oxide to reagent grade orthophosphoric acid. Each acid was heated in a sealed borosilicate glass container to 350° C. in 20 minutes and held at 350° C. another 10 minutes to equilibrate the phosphate species. Both acids then had the same P₂O₅ content and the equilibrium distribution of species within the limits of error of chromatographic analysis. The compositions of the acids are listed in Table I.

Procedure

The bomb was charged with a weighed amount of superphosphoric acid and heated to the base temperature. The calorimeter then was calibrated electrically, ammonia was added to give a

Table I. Initial and Ammoniated Superphosphoric Acids

Sample	Composition, %				Distribution, % of P ^a					
	N	P	NH ₃	P ₂ O ₅	Ortho	Pyro	Tri	Tetra	Penta	Other
A										
Initial	0.0	33.23	0.0	76.15	61.8
Final	3.7	31.74	4.5	72.73
B										
Initial	0.0	33.12	0.0	75.88	50.8	40.2	7.3	1.2	...	0.5
Final	9.8	29.17	11.9	66.85	52.4	32.2	10.6	3.2	...	0.6
C										
Initial	0.0	33.12	0.0	75.88	49.1	39.3	8.6	2.2	...	0.8
Final	11.4	28.14	13.9	64.49	50.7	34.6	9.7	3.4	0.9	0.5
Equilibrium (5, 6)	0.0	33.17	0.0	76.00	49.0	42.8	7.1	1.0	0.1	0.02

^a After ortho- and pyrophosphates, prefixes denote *n* in formula H_{n+2}P_nO_{3n+1}; "other" denotes species too large to move on chromatographic paper.

temperature rise of 5° to 10° C., and the calorimeter was again calibrated electrically. The average of the two calibrations was taken as the energy equivalent of the calorimeter. Corrections to the observed temperature rise for the electrical calibrations and the heat of reaction were made by a published method (3).

The temperature of the ammonia gas immediately before admittance to the bomb was measured with a thermocouple. A sensible-heat correction was made for the difference between the temperature of the entering gas and the average temperature during the reaction period—the heat content of ammonia was taken from published data (6). The amount of ammonia added was determined by weighing the supply tank before and after each run.

In each series of runs, the initial acid (about 400 grams) was ammoniated in several successive steps (each about 7 grams of NH₃) and the product of one run was the starting material for the next. The results are reported in Table II as the integral heats of reaction—that is, as the heat evolved when the initial acid is ammoniated to the final composition of each run.

Results and Discussion

In the TVA pilot plant, superphosphoric acid is ammoniated at 200° C. to 5.8 to 6.2 pounds of NH₃ per 20 pounds of P₂O₅. In the calorimeter runs the ammoniation proceeded smoothly to saturation at each base temperature, but the ammonia content at saturation increased markedly with increase in the base temperature, as shown in Table II. In runs below saturation, the ammonia pressure in the bomb was held at about 5 p.s.i.g. at base temperatures of 100° and 125° C. and at about 10 p.s.i.g. at the base temperature of 180° C. As saturation was approached, the ammonia pressure was increased, with only slight effect on the rate of ammoniation, and at saturation the ammonia pressure in the bomb reached a maximum of 27 p.s.i.g.

The lack of equilibration of acid *A* before ammoniation had no measurable effect on either the heat of ammoniation or the capacity of the acid to absorb ammonia. After the three runs with this acid to saturation at 100° C. reported in Table II, the partially ammoniated acid was heated to 125° C. and ammoniation was continued in three more runs (not reported) until the uptake of ammonia virtually ceased. The final concentration, 3.48 pounds of NH₃ per 20 pounds of P₂O₅, is in close agreement with that obtained with acid *B*, so that the effect of temperature on both the uptake of ammonia and the heat of ammoniation is real and not the result of differences in the initial acids.

As shown in Table I, ammoniation caused small but definite shifts in the distribution of the phosphate species. Pyrophosphate decreased, and all other species increased slightly.

Table II. Heat of Ammoniation of Superphosphoric Acid

Acid Sample	Temp., ° C.		Ammoniation, Lb. NH ₃ /20 Lb. P ₂ O ₅	Integral Heat, ^a B.t.u./Lb. NH ₃		
	Base	Av.				
A	100	115	0.67	3634		
		110	1.13	3553		
		104	1.24	3548		
		137	0.39	3547		
B	125	138	0.82	3496		
		136	1.12	3441		
		137	1.52	3373		
		138	2.00	3285		
		137	2.46	3191		
		136	2.97	3107		
		136	3.54	3023		
		126	3.56	3023 ^b		
		C	180	190	0.39	3458
				192	0.88	3393
193	1.34			3321		
192	1.80			3244		
192	2.31			3167		
191	2.77			3093		
192	3.33			3007		
191	3.85			2930		
190	4.28	2874				
185	4.37	2862				

^a Total heat that would be evolved in ammoniating fresh acid to indicated degree.

^b Ammoniation too slight to give significant temperature rise.

Corrosion of the bomb was slight at 100° and 125° C. and more apparent at 180° C. The product of the runs at 125° C. was white and contained less than 0.01% Ni, whereas the product of the runs at 180° C. was green and contained 0.2% Ni and 0.2% Fe, but no Cr. The effect of the corrosion is considered to be less than the experimental error of the measurements.

Over the range 180° to 200° C. measurements of the heat capacities of the empty bomb and of the bomb filled with acid *C* showed that, for the unammoniated acid

$$c = 0.262 + 0.00126t$$

where *c* = specific heat of unammoniated acid, calories per gram per °C., and *t* = temperature, °C.

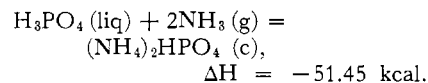
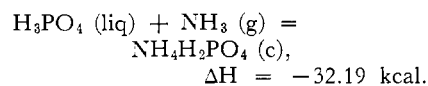
From the heat capacity of the empty bomb and the electrical calibrations after each step of ammoniation at the base temperature of 180° C., for the partially ammoniated product at 196° C.

$$c = 0.530 + 0.0076N$$

where *c* = specific heat of product, calories per gram per °C., and *N* = degree of ammoniation, pounds of NH₃ per 20 pounds of P₂O₅. This equation fits the experimental data with an average deviation of 0.24%.

The major crystalline components of pilot-plant ammonium polyphosphates are monoammonium orthophosphate and triammonium pyrophosphate. The crystallite size and relative abundance of these phases are influenced by the conditions of the ammoniation and subsequent granulation. Petrographic and x-ray examination of the products of this work, however, showed only monoammonium orthophosphate as a crystalline phase; other components were present as amorphous materials, and the fluid product set up as a gel on cooling.

Similar measurements have not been made of the heat of ammoniation of orthophosphoric acid, but published data (7) show the following heats of reaction at 25° C.



In engineering units, these heats of reaction are 3402 B.t.u. per pound of NH₃ at 4.8 pounds of NH₃ per 20 pounds of P₂O₅ for NH₄H₂PO₄, and 2719 B.t.u. per pound of NH₃ at 9.6 pounds of NH₃ per 20 pounds of P₂O₅ for (NH₄)₂HPO₄. With allowances for differences in the base temperatures, these heats of reaction are in agreement with those obtained in the present work.

Literature Cited

- (1) Farr, T. D., Tennessee Valley Authority, Wilson Dam, Ala., Chem. Eng. Rept. 8 (1950).
- (2) Getsinger, J. G., Siegel, M. R., Mann, H. C., Jr., J. AGR. FOOD CHEM. 10, 341 (1962).
- (3) Hubbard, W. N., Scott, D. W., Waddington, G., "Experimental Thermochemistry," Chap. 5, F. D. Rossini, ed., Interscience, New York, 1956.
- (4) Huhti, A. L., Gartaganis, P. A., Can. J. Chem. 34, 785 (1956).
- (5) Jameson, R. F., J. Chem. Soc. 1959, p. 752.
- (6) National Bureau of Standards, "Table of Thermodynamic Properties of Ammonia," Circ. 142 (1923).
- (7) Slack, A. V., Farm Chem. 125, 16 (1962).

Received for review July 6, 1964. Accepted October 26, 1964. Division of Fertilizer and Soil Chemistry, 148th Meeting, ACS, Chicago, Ill., September 1964.