equation is —27.72. This value gives for the standard entropy of phosphine the value 52.4 entropy units.

If $-R \ln K$ is plotted against $1/T$, the slope of the curve is ΔH. This was done on a large scale plot between the limits 573°K. and 613°K. The points were somewhat scattered. A line drawn through the means of these points had a slope of —20,200 as compared with the value —19,711 cal., calculated from the equation for the heat of reaction.

In conclusion the author wishes to thank Dr. R. K. McAlpine for his kind help and encouragement in this investigation. Acknowledgment is also due to Mr. L. D. Anderson of the Riverton High School for his kindness in lending some of the apparatus used in these experiments.

Summary

1. The equations have been worked out for the free-energy change of fusion and vaporization of white phosphorus. The standard free energies of these changes have been calculated.

2. The dissociation of phosphine has been measured in the temperature interval 573°K. to 613°K. From this the free energy of formation of phosphine has been calculated.

3. The entropy change of vaporization and fusion and the standard entropy of phosphorus have been calculated. The standard entropy of phosphine has been calculated.

RIVERTON, WYOMING

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MACDONALD COLLEGE]

DISSOCIATION PRESSURES OF AMMONIUM ORTHOPHOSPHATES[1]

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Recent developments in the manufacture of ammonia[2] and phosphoric acid[3] have demonstrated the possibility of the commercial use of ammonium phosphate as a fertilizer. As such it contains two of the fundamental plant nutrients in readily available form.[4]

The most economical starting state for ammonia is the gaseous and for phosphoric acid a concentrated solution, the latter because the heat of reaction is sufficient to dry the product. The various reactions of ammonia gas with phosphoric acid have been the subject of the following experiments made by the author.

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[1] From a thesis submitted in partial fulfilment of the requirements for the degree of M. Sc. in McGill University.

[2] Brown, *Trans. Am. Electrochem. Soc.*, **48**, 175–182 (1925).

[3] Jacob, *ibid.*, **48**, 125–133 (1925).

[4] Allison, *Soil Science*, **5**, 1–80 (1918).

Knowing the dissociation pressures of ammonia over saturated solutions of mono- and di-ammonium phosphates it is possible to prepare a gas mixture with a partial pressure of ammonia lying between these values. By passing this mixture into phosphoric acid, mono-ammonium phosphate can be formed without producing any di-ammonium phosphate, even though the passage of gas is continued after all of the free phosphoric acid has been neutralized. A similar process is, of course, applicable to the manufacture of the di- and tribasic salts in the pure, dry state.

Mono-ammonium phosphate crystals made by the rapid neutralization of concentrated phosphoric acid contain hygroscopic, occluded acid. This may be neutralized without the formation of di-ammonium phosphate by drying with an air-ammonia mixture as mentioned above.

Since mono-, di- and tri-ammonium phosphates are made by the precipitation of the salts from saturated solutions, concentration is not a variable. Accordingly, the dissociation pressures were determined with the dry, powdered salts which, from thermodynamic reasoning, must have the same dissociation pressures as the saturated solutions. The temperature range of the measurements, 80–125°, was chosen to include the zone of precipitation and drying.

Materials

The mono-ammonium phosphate used in the determination of the dissociation pressure was Merck's c. p. This salt in solution was slightly acid to methyl red and was heated for several hours before using to dissociate any di-ammonium phosphate which may have been present. In this connection the author was misled by a preliminary experiment made with Kahlbaum's c. p. mono-ammonium phosphate which contained some of the secondary salt and in solution was neutral to methyl red.

The di-ammonium phosphate used in the measurements was Baker's c. p. It contained none of the tribasic salt.

No attempt was made to dry the two salts completely because moisture does not interfere with the air-saturation method of vapor pressure determinations.

Experimental

Measurements of the partial pressure of ammonia over mono- and di-ammonium phosphates were made with a type of air-saturation apparatus. A measured amount of air was passed at a uniform rate through a purifying train of soda lime and phosphorus pentoxide and thence to a constant-temperature well containing alternate layers of the finely powdered salt and glass wool. The gas then bubbled through an absorbing worm containing an excess of standard sulfuric acid. At the end of the run the excess acid was titrated and the partial pressure of ammonia calculated. The constant-temperature well was vapor-jacketed and benzene, water, toluene, *n*-butyl alcohol and amyl alcohol were used for heating. The temperature could be controlled to 0.02° for the duration of a determination (about 2 hours) and the powder within the well was uniformly heated to the boiling point of the heating liquid. That equilibrium was reached was proved by making several runs at different rates for each temperature.

At 100° mono-ammonium phosphate had so small a dissociation pressure that it could not be measured, and even at 125° the pressure was only 0.05 mm.

The results of the di-ammonium phosphate experiments are shown in Table I.

Table I

Dissociation Pressure of Di-ammonium Phosphate

Temp., °C.	1/Abs. temp.	Dissoc. press., mm. Hg
80.24	0.002830	1.36
99.91	.002680	5.02
109.30	.002615	11.00
116.89	.002564	17.74
125.36	.002509	29.35

A plot of the logarithm of the dissociation pressures of di-ammonium phosphate against the reciprocals of the corresponding absolute temperatures is given in Fig. 1. Substituting values from the straight line of Fig. 1 in the equation

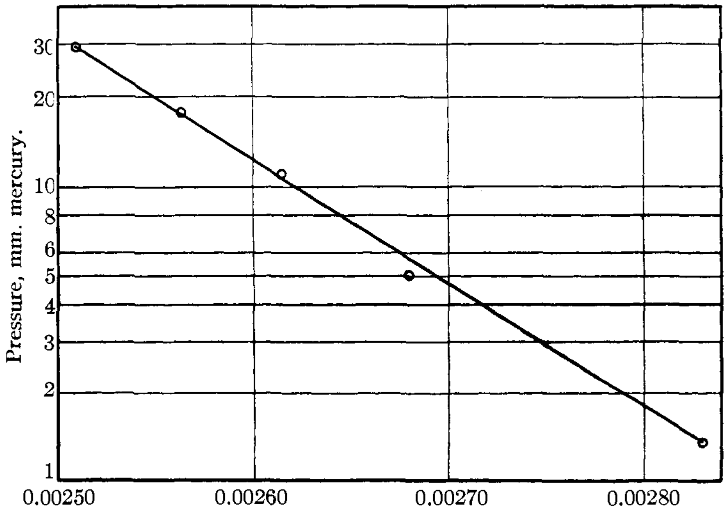

Fig. 1.—Dissociation pressures of ammonium phosphate.

$$(ln\ K_1 - ln\ K_2) = \frac{DH}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (1)$$

the heat of reaction for the equation

$$\underset{\text{solid}}{(NH_4)_2HPO_4} = \underset{\text{gas}}{NH_3} + \underset{\text{solid}}{NH_4H_2PO_4} \qquad (2)$$

is found to be 19,050 calories.

From Kopp's[5] law the molal heat capacity of ammonia in a solid is 13.3 calories per mole, while in the gas phase[6] it is given by the equation $8.04 - 0.0007T + 0.0000051T^2$. Hence the molal heat capacity of the products of equation (2) at 373°K. is $13.3 - 9.1 = 4.3$ calories less than that of reacting substances, and the heat of reaction is $4.3 \times 45 = 194$ calories greater at 80° than at 125°. Since this would make the curve in Fig. 1 concave to the origin, with a curvature of 1 per cent., the experimental values for four of the points are in nice agreement. The point corresponding to 100° lies below the curve and the discrepancy is not within the limit of experimental error. The standard solutions, volumetric apparatus and thermometers were used in the other measurements and carefully evaluated and the point is the arithmetic mean of six separate determinations, of which none varies more than 2 per cent. of its value from the mean.

The dissociation pressure of tri-ammonium phosphate was too great to measure in the air-saturation apparatus so the determinations were made by the static method. They are less accurate than those of the di-ammonium phosphate because of difficulties introduced by water formation, possibly from the production of some metaphosphate at high temperatures, and slowness of absorption at pressures lower than atmospheric.

Since dry tri-ammonium phosphate was not purchasable, it was prepared from the dibasic salt in the apparatus itself by passing ammonia at 100° and 1 atmosphere pressure over it. The tube containing the dry tri-ammonium phosphate was then attached through a mercury seal to a mercury manometer and a current of pure dry ammonia gas bubbled over it and through the manometer. When the salt and the apparatus were dry and free from any foreign gas the tube was sealed off at a constriction.

Because of the prementioned difficulty of slow absorption, only points near or above atmospheric pressure were determined, and such lower values as were needed were found by extrapolation.

The values obtained are given in Table II. In view of their small number their accuracy justifies only an approximate calculation of the heat of reaction. Calculated as before, its value is 9400 calories for the reaction

$$\underset{\text{solid}}{(NH_4)_3PO_4} = \underset{\text{solid}}{(NH_4)_2HPO_4} + \underset{\text{gas}}{NH_3} \qquad (3)$$

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[5] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, **1923**, p. 77 [6.4 + 3 (2.3) = 13.3].

[6] *Ibid.*, p. 80.

TABLE II

DISSOCIATION PRESSURES OF TRI-AMMONIUM PHOSPHATE

Temp., °C.	Dissoc. press., mm. Hg
110.1	733.1
116.5	825.7
125	1177

To check the vapor-pressure determinations, pure mono-ammonium phosphate was prepared by passing a large excess of a 1 per cent. ammonia-air mixture through concentrated phosphoric acid at 110°. The product had a dissociation pressure of ammonia corresponding to mono-ammonium phosphate and in solution at 110° would absorb no ammonia from the 1 per cent. mixture. A product having the dissociation pressure of di-ammonium phosphate was obtained by lowering the temperature to 100° while the 1 per cent. mixture was passed through. Pure, dry tri-ammonium phosphate was made by treating di-ammonium phosphate at 100° with ammonia at 1 atmosphere pressure.

The writer wishes to thank Dr. Milton Hersey of Montreal for a scholarship which rendered the research possible and Dr. J. F. Snell for supervision and for the facilities afforded in Macdonald College.

Summary

The reactions of gaseous ammonia and phosphoric acid solutions have been studied in order to produce the three ammonium salts of phosphoric acid in a pure state.

To produce the desired salt with the exclusion of the others, a variation in the partial pressure of the ammonia gas was used. This necessitated the determination of the dissociation pressures of mono-, di- and tri-ammonium phosphates. The pressure of mono-ammonium phosphate over the range 80–125° was less than 0.05 mm.; that of di-ammonium phosphate was 1.4 mm. at 80° and 30 mm. at 125°. The partial pressure of tri-ammonium phosphate, determined less accurately, was 730 mm. at 110° and 1170 mm. at 125°.

Using the partial-pressure method, pure mono-, di- and tri-ammonium phosphates were prepared.

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