[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Dissociation Pressures of Magnesium Ammonium Phosphate Hexahydrate and Some Related Substances. VII

BY SAMUEL J. KIEHL AND HENRY B. HARDT

In 1847 Heintz[1] published a method for the determination of magnesium or phosphorus based upon the precipitation of these elements as magnesium ammonium phosphate hexahydrate and the ignition of it to magnesium pyrophosphate. This method, as improved by Gibbs[2] in 1873, has come into very general use. It was and is, however, subject to a large number of possible errors, and there have appeared, therefore, in the last sixty years ninety or more research reports upon its various phases. The facts brought out by these studies fall mainly into two groups: those dealing with the conditions necessary to the quantitative precipitation of the magnesium or phosphorus in the form of pure $MgNH_4PO_4 \cdot 6H_2O$; and those dealing with the ignition of this precipitate to $Mg_2P_2O_7$. The subject has been attacked from almost every conceivable angle.

Nevertheless there remains still a need for some information which may be deemed important for the ignition of the hexahydrate. It seems noteworthy that, although the salt precipitated is a hydrate which loses its water of hydration during the ignition process, there should be a lack of information upon its dissociation pressure. Furthermore, it is not only a hydrated ammonium salt which loses both its water of hydration and its ammonia, but also an orthophosphate which is converted to a pyrophosphate by the loss of water of constitution. Consequently we believe that a knowledge of the pressure developed in the reactions involved during heating will help to ensure an intelligent manipulation of an operation which is so vital a part of a quantitative procedure.

It seems probable, therefore, that a study of the dissociation of magnesium ammonium phosphate from the viewpoint of the phase rule may yield valuable information. According to the phase rule, a salt hydrate that dissociates into a lower hydrate or an anhydrous salt and a gaseous phase is a two-component system, and with three phases present it is univariant. A large number of such systems have been studied and reported in the literature by a number of very able investigators. Among those who have done much in this field to improve the method for measuring dissociation pressures of such systems are: Johnston,[3] whose excellent apparatus and method present a real improvement, Baxter and Lansing, Frowein, Menzies and Wilson.[4] The last two mentioned give good criticisms of the

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[1] Heintz, *Pogg. Ann.*, **73**, 137 (1847).

[2] Gibbs, *Am. J. Sci.*, [3] **5**, 115 (1873).

[3] Johnston, *Z. physik. Chem.*, **62**, 330 (1908).

[4] Baxter and Lansing, THIS JOURNAL, **42**, 419 (1920); Frowein, *Z. physik. Chem.*, **1**, 5 (1887); Menzies, THIS JOURNAL, **42**, 1952 (1920); Wilson, *ibid.*, **43**, 704 (1921).

many preceding researches and list the errors often made in manipulation and measurement.

The studies referred to above deal with univariant systems. Magnesium ammonium phosphate hexahydrate also forms such a system when it dissociates into a lower hydrate and water. However, in its case there is a further dissociation which yields a magnesium acid phosphate and ammonia and forms a third solid phase and a third component. This system, consisting of three components present in four phases, is also univariant and has, therefore, a definite dissociation pressure at any fixed temperature: Therefore both the two-component and three-component systems are represented in this investigation. Systems 1, 4 and 5 listed below consist of two components, while systems 2 and 3 contain three components. The following systems were studied

System 1. $MgNH_4PO_4{\cdot}6H_2O$, $MgNH_4PO_4{\cdot}H_2O$, H_2O
System 2. $MgNH_4PO_4{\cdot}6H_2O$, $MgNH_4PO_4{\cdot}H_2O$, $MgHPO_4{\cdot}3H_2O$, H_2O, NH_3
System 3. $MgNH_4PO_4{\cdot}H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O
System 4. $MgHPO_4{\cdot}7H_2O$, $MgHPO_4{\cdot}3H_2O$, H_2O
System 5. $MgHPO_4{\cdot}3H_2O$, $MgHPO_4{\cdot}H_2O$, H_2O

Preparation and Analysis of Materials

$MgNH_4PO_4{\cdot}6H_2O$.—Equivalents of $Na_2HPO_4{\cdot}12H_2O$, carefully purified. and magnesia mixture (usually about one liter of each, of one-tenth molar concentration), were mixed and the precipitate dissolved in hydrochloric acid. Very dilute ammonium hydroxide was then added slowly with constant stirring until the salt was almost all precipitated. Then more concentrated ammonium hydroxide was added until its concentration was approximately one molar. After standing for four hours or more, it was washed with water until a sample of it dissolved in one-tenth molar nitric acid gave no test for chloride with siliver nitrate. After it was filtered on a hardened filter paper in a Buchner funnel and washed with four 50-cc. portions of absolute ethyl alcohol, then with four 50-cc. portions of anhydrous ether, it was transferred to a bottle where suction was applied by means of an oil pump for an hour. The salt adhering to the filter paper was rejected to reduce the danger of organic impurities. By this method a number of lots were prepared, all of which were shown by the microscope to be distinctly and uniformly crystalline, gave the theoretical loss in weight on ignition closer than one part per thousand, gave the theoretical percentage of ammonia within one part per thousand and gave snow-white residues on ignition.

$MgNH_4PO_4{\cdot}H_2O$.—This salt was prepared by the same method as the hexahydrate, except that it was precipitated from boiling solution, kept in an oven in the mother liquid at 100–102° for twenty-four hours, washed with boiling water, and dried in an oven at 106° for eight hours. It was very uniformly crystalline, consisting of square, flat crystals, gave the theoretical loss in weight upon ignition, the theoretical ammonia content, and snow-white residues upon ignition.

$MgHPO_4{\cdot}7H_2O$.—Equivalents of $MgSO_4{\cdot}7H_2O$ and $Na_2HPO_4{\cdot}12H_2O$ in solutions were mixed; the precipitate was dissolved by adding a small amount of sulfuric acid, and reprecipitated by adding slowly a dilute sodium hydroxide solution. The salt was washed with water, alcohol and ether, dried on a glass plate until free from ether, and bottled. It consisted of large needle-shaped crystals which gave the theoretical loss of weight upon ignition. This hydrate is very unstable. Further comment will be made later.

$MgHPO_4\cdot 3H_2O$.—When the $MgHPO_4\cdot 7H_2O$ still in its mother liquid was warmed to 35°, the long needle-like crystals changed to the rhombic form. Upon ignition these gave the theoretical loss in weight for the reaction $2MgHPO_4\cdot 3H_2O \rightleftarrows Mg_2P_2O_7 + 7H_2O$ and a snow-white residue.

Apparatus

The apparatus used for the measurement of pressures is an adaptation of that of Kiehl and Wallace,[5] which was a modification of that of Johnston.[3] Some of the systems, in fact, may well be measured with practically the same arrangement. The first salt studied, $MgNH_4PO_4\cdot 6H_2O$, however, has such an exceptionally high dissociation pressure that with this form of apparatus it was impossible to prevent the condensation of the water. The water vapor pressure produced was so near that of water itself that even a slight difference of temperature between the furnace and the steam-jacket caused condensation in the cooler portion of the system within the steam-jacket.

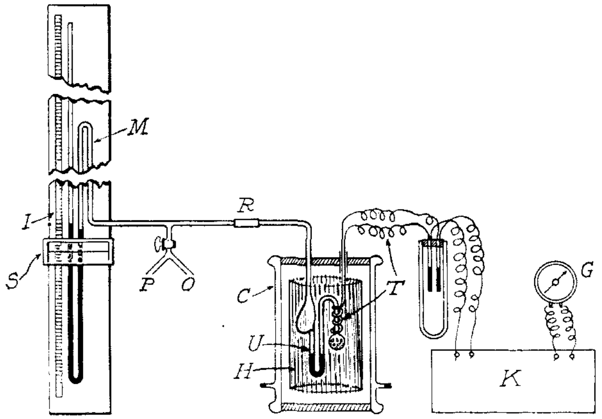

Fig. 1A.—Apparatus for the measurement of dissociation pressures.

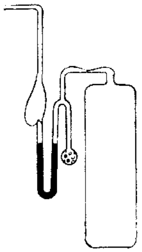

Fig. 1B.—Modified manometer used in determining the ratio of water to ammonia in the vapor phase.

A modification was made, therefore, whereby this condensation was prevented, the arrangement was simplified, and manipulation made much easier. The essentials of the apparatus are shown in Fig. 1A. The furnace and steam-jacket formerly used were combined into a unit consisting almost entirely of Pyrex glass and a resistance wire. A double-walled cylinder, C, of heavy Pyrex glass, with a vacuum between the walls, 27 centimeters long and 6.5 centimeters inside diameter was used as a chamber for the heater. The ends were closed with corks covered with heavy asbestos paper. The heating unit, H, consisted of a smaller Pyrex cylinder upon which was wound 27 feet of 28-gage nichrome wire. When this heater was connected with the 110-volt circuit, any temperature from room temperature up to 425° could be secured by use of appropriate resistance.

The manometer, M, described heretofore,[5] was connected to an oil pump, by which a vacuum of 0.2 mm. pressure could be secured. When pressures less than one atmosphere were to be measured, an air valve at O was used to admit air to counterbalance the pressures developed by the system; and for pressures greater than an atmosphere and for

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(5) **Kiehl** and Wallace, THIS JOURNAL, **49**, 375 (1927).

Wood's metal as a confining liquid, O was connected to a high-pressure hydrogen cylinder by means of heavy-walled rubber tubing which was wrapped tightly with tire-tape. The connection, R, was also wrapped pressure tubing, which permitted tilting the furnace after evacuation. Before it was wrapped the rubber tubing was thoroughly massaged several times, inside and out, with warm castor oil, to make it less permeable to gases. This oiled and wrapped pressure tubing retained pressures of five and one-half atmospheres satisfactorily.

As a confining liquid for the gases formed by the dissociation, mercury is usually the best because it is the least likely to absorb or react with the gases present. In this investigation it was found very satisfactory for low temperatures. Since the nature of the systems measured and the method and apparatus used required the confining liquid to be kept at the same temperature as the system itself, and since mercury boils at 357°, a large correction due to the vapor pressure of mercury thereupon would be required as the temperature approached this point. Besides, as the temperature rose, the mercury would distil from the capillary and condense in the cooler portion of the tube.

In looking for a confining liquid that did not have this limitation at higher temperatures, Wood's metal proved to be excellently suited. It has practically no vapor pressure at the temperatures where its use was required. When a sample of the purest material obtainable was placed alone in the dissociation pressure apparatus no appreciable pressure developed at even the highest temperature used for measuring dissociation pressures. When, however, the temperature was increased to 300°, a pressure of 5 millimeters was developed. Two limitations should be mentioned in connection with its use. At higher temperatures especially, a troublesome scum will form upon the surface of the metal if air is allowed to come in contact with it. Hydrogen was therefore used to counterbalance the pressure developed in the system. The metal should not be allowed to solidify in the capillary as the strain produced by the contraction of the cooling glass and by the solidification of the metal may break the small manometer. After the completion of the experiment the metal in the liquid state may be transferred to the properly constructed reservoir.

A chromium-plated strip of brass 1.9 cm. wide by 7.6 cm. long with a millimeter scale engraved upon it was attached to the legs of the differential manometer within the heater to aid in leveling the confining liquid.

For reading temperatures up to 350° a copper–constantan thermocouple was employed. Above that temperature a platinum–platinum-rhodium thermocouple was used. The thermocouples were standardized against the melting points of samples of tin, lead. zinc and aluminum from the United States Bureau of Standards, the boiling points of water, alcohol and ether and the freezing point of water. A water and ice cold junction was used. The instruments and method of measurement were described heretofore.[5]

For heating the salts *in vacuo*, a thick-walled Pyrex tube 40 cm. in length and 5 cm. in diameter, with a ground-glass cap which was fitted with a stopcock, was used. The lower third was placed in an electric furnace and the upper part protected from the heat of the furnace by two tightly fitting asbestos stoppers, so that when evacuated the lower part could be heated to above 450° while the upper end remained at room temperature. A platinum crucible containing the salt was lowered into the tube by means of a glass rod bent at the bottom into the form of a ring.

For the ignition, when they were required, porcelain Gooch crucibles were used in an electrically heated muffle-furnace.

Method

Dissociation Pressures.—The well-known static method for measuring dissociation pressures of salt hydrates was employed. The bulb, filled with a sufficiently large sample of the salt (0.1 to 0.25 g.) was sealed to the small manometer. When mercury was used as a confining liquid it was poured into the reservoir, and the manometer connected at R. The system was then evacuated and left overnight. The next morning the system was again evacuated and the mercury tilted into the capillary. Then the heat was turned on and the desired temperature maintained until the pressure became constant. All reactions attained equilibrium in a reasonable time; the longest time required was about sixty hours, in the case of System 1 at low temperatures, which was unusual. When Wood's metal was used the procedure was exactly the same except that the system was heated to 75–100° before the liquid was introduced. When constant pressure had been reached and maintained without change for an hour or more it was recorded; the temperature was then increased and the new equilibrium pressure found. When the highest pressure to be measured had been determined, the process was reversed; that is, the temperature was reduced stepwise, and the pressure found for each temperature. The temperature–pressure curve was considered a true equilibrium curve only when the curve for increasing temperatures coincided with that for decreasing temperatures. The same equilibrium pressure therefore was obtained when approached from either lower or higher temperatures.

The entire experiment was then repeated with a mixture of the substance being studied and the solid phase or phases believed to have formed during dissociation. When no irregular behavior from the beginning throughout the temperature range occurred and when the curve thus obtained was the same as that for the original salt alone, evidence for the identity of the solid phase was established and the equilibrium curve confirmed.

Evidence for Phases Present

Since no distinctive tests are known by which the hydrates of $MgNH_4PO_4$ and of $MgHPO_4$ may be identified when in the presence of each other, it is necessary to establish the presence of all phases by reasoning from the results obtained. The evidence showing which substances are formed by the dissociation in each system is given below.

System 1. $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O

1. The monohydrate is formed from the hexahydrate and it may be isolated in fairly pure form if the gas evolved at 50° or less is removed as it is liberated.

2. Red litmus in the reaction chamber does not change to blue below 50°, nor does it change when moistened and exposed to the gas which has been removed from the reaction chamber. Ammonia is not given off below 50°.

3. The hexahydrate forms monohydrate because the two when mixed give the same curve as the hexahydrate alone.

System 2. $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O, NH_3

1. The monohydrate is formed from the hexahydrate and it may be isolated in fairly pure form if the gas evolved at 50° or less is removed as fast as it is formed.

2. $MgNH_4PO_4 \cdot H_2O$, when heated in a closed system under the high vapor pressure of water furnished by the hexahydrate, first loses ammonia, forming $MgHPO_4 \cdot H_2O$ (see System 3), but under the conditions prevailing here, the monohydrate is converted to the trihydrate, because the trihydrate is the salt in whose range of existence the pressure–temperature curve for System 2 lies.

3. The water and ammonia, on cooling, form a solution which quickly turns red litmus blue, and smells strongly of ammonia.

4. A mixture of the first and second, or first, second and third, solid phases gives the same curve as the first alone.

System 3. $MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3. H_2O

1. Either zinc acetate reagent or silver nitrate gives tests for pyrophosphate[6] whenever both ammonia and water are found in the gaseous phase.

2. When $MgNH_4PO_4 \cdot H_2O$ is heated in an open vessel so as to drive off a part of the volatile matter, it always retains a larger percentage of its NH_3 than of its H_2O as shown below:

Temp. to which heated, °C.	340	335	350	380
NH_3 retained, %	24.5	29.5	17.0	6.0
H_2O retained, %	17.3	24.0	12.0	2.0

This shows that the water of hydration may be expelled while some of the ammonia still remains in the form of anhydrous ammonium salt.

3. When $MgNH_4PO_4 \cdot H_2O$ is heated in the temperature–pressure apparatus, and the gaseous phase *at equilibrium* is analyzed, the ratio of water to ammonia is found to be about 3 : 1. Data are tabulated under "Experimental Results." These analyses show that some of the substance which has lost water has not lost ammonia. Each molecule of $MgNH_4PO_4 \cdot H_2O$ contains but one molecule of water of hydration for every molecule of ammonia.

4. The system at equilibrium always gives positive tests for pyrophosphate whenever ammonia is present.

5. Mixtures of the first and second, or first, second and third, phases give the same pressure–temperature curve as the first alone.

System 4. $MgHPO_4 \cdot 7H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O

1. If the vapors formed are pumped off, it is found that there is a great decrease in pressure at equilibrium when the composition of the resulting solid is approximately $MgHPO_4 \cdot 3H_2O$.

2. Crystals appear which have the same form as those of pure $MgHPO_4 \cdot 3H_2O$.

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(6) Kiehl and Coats, THIS JOURNAL, **49**, 2180 (1927).

3. Either the heptahydrate or a mixture of the two hydrates gives the same curve.

System 5. $MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, H_2O

1. Zinc acetate reagent does not give a test for pyrophosphate even when a great pressure has been developed. (This reagent, consisting of a thirty-two hundredths molar zinc acetate solution in the presence of one-eighth its volume of glacial acetic acid, has been shown by Kiehl and Coats[7] to be sufficiently sensitive to detect 0.0006 molar pyrophosphate in the presence of 0.1 molar orthophosphate.
2. If the vapors formed are pumped off, it is found that there is a great decrease in equilibrium pressure when the composition of the resulting solid is approximately $MgHPO_4 \cdot H_2O$.

Determining the Ratio of Water to Ammonia.—To determine the ratio of water to ammonia in System 3 where both of these substances are liberated as gases, the following method was used. A receptacle resembling a large test-tube was sealed to the bulb containing the salt as shown in Fig. 1B. There was a constriction in the tube which connected the bulb to the remainder of the apparatus to facilitate sealing off the bulb when equilibrium was established. In addition to the regular stopper in the top of the furnace, an extra asbestos stopper with a small hole just over the constriction in the tube was used.

The apparatus was arranged in the usual way except that the salt bulb contained about a gram of salt instead of the usual 0.2 to 0.3 g. charge. When equilibrium was established the temperature was noted, the extra stopper of the furnace removed, and the large bulb quickly sealed off with a small, hot flame. This could be done with practically no change in temperature, and with the leveling liquid showing no change in position. The bulb was then inserted into a measured volume of 0.02 *N* sulfuric acid and the tip broken off. The excess acid was back-titrated with 0.02 *N* sodium hydroxide and the standard volume of the ammonia as a gas was calculated. The standard volume of all the gas present was also calculated and the water determined by difference. The method worked very satisfactorily up to a total pressure of one atmosphere.

Experimental Results

The temperature–pressure data for four runs on each system studied are given in the following tables. All pressures are recorded in millimeters of mercury at 0°.

In order to select from the temperature–pressure data recorded above those values which would as nearly as possible represent the value most probable for each temperature in each system, the following method was used. From the data for each of the four runs a curve was drawn; from these four curves, one pressure corresponding to the average of the four

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(7) Ref. 6, p. 419.

TABLE I

EXPERIMENTAL DATA FOR SYSTEMS 1 AND 2

$MgNH_4PO_4{\cdot}6H_2O$, $MgNH_4PO_4{\cdot}H_2O$, H_2O (below 60°)
$MgNH_4PO_4{\cdot}6H_2O$, $MgNH_4PO_4{\cdot}H_2O$, $MgHPO_4{\cdot}3H_2O$, H_2O, NH_3 (above 60°)

Run no. 1		2		3		4	
T, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*, °C.	*P*, mm.
41.1	34.2	39.0	32.1	40.0	35.0	42.3	34.9
50.0	71.1	51.9	83.0	51.6	77.0	55.5	79.9
53.5	78.2	59.0	100.0	55.4	89.3	57.0	88.9
62.0	122.5	59.9	113.0	59.0	106.3	61.5	117.5
65.0	144.8	63.6	133.4	61.5	121.4	66.0	139.5
73.0	205.1	65.0	154.8	62.8	126.7	77.1	275.4
85.0	377.9	71.2	196.2	68.1	162.1	86.0	390.6
87.0	407.9	75.0	242.2	69.2	169.9	102.5	710.1
89.5	450.7	88.3	450.8	74.0	220.0	118.9	1208.1
94.0	513.0	100.1	670.1	81.9	292.2	119.6	1240.8
108.0	846.8	106.2	823.0	88.5	373.4	132.0	1809.8
112.5	957.0	115.2	1020.0	89.6	423.2	133.6	1941.5
125.6	1423.0	125.6	1448.8	102.2	704.6	135.1	2008.0
128.5	1620.0	137.0	2113.3	103.4	713.9	139.6	2264.1
131.0	1734.0	140.5	2271.7	111.9	948.8	146.0	2536.0
132.5	1838.0	146.2	2655.0	112.6	952.6	152.8	3273.3
134.8	1926.0	152.4	3263.3	118.0	1151.1		
136.5	1950.0	156.2	3696.7	120.0	1238.7		
150.0	2846.0			120.5	1278.9		
152.8	3423.0			134.4	1969.9		
				140.5	2352.0		
				142.6	2385.0		
				159.1	3834.0		

TABLE II

EXPERIMENTAL DATA FOR SYSTEM 3

$MgNH_4PO_4{\cdot}H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O

Run no. 1		2		3		4	
T, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*, °C.	*P*, mm.
121.9	9.0	131.7	11.1	127.8	9.8	125.0	9.5
131.0	11.1	145.5	18.9	131.9	12.2	132.7	14.7
165.0	52.8	152.8	24.9	137.4	13.9	138.0	17.5
209.8	217.4	159.9	35.0	149.1	22.5	163.8	45.3
227.5	353.3	183.6	87.4	164.8	43.9	175.1	64.8
246.5	684.9	198.7	141.0	175.7	62.8	186.6	90.8
253.3	908.5	227.0	311.8	188.4	97.2	195.1	136.2
261.6	1280.0	250.2	735.4	199.2	143.8	203.0	174.5
270.8	1888.0	265.0	1389.0	210.7	207.7	215.5	235.8
279.9	2873.4	270.0	1839.6	231.0	369.1	230.9	392.0
280.9	3187.4	274.9	2400.0	250.0	767.5	258.9	1145.0
281.9	3429.4	279.1	2929.0	254.8	1117.0	272.8	2209.0
				274.0	2514.2	279.5	3089.0
				281.6	3327.2		

values, one for each curve taken at ten degree intervals was obtained. From these average values recorded in Table IV, the final curve in Fig. 2 for the system was drawn.

TABLE III

EXPERIMENTAL DATA FOR SYSTEM 5

$MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, H_2O

Run no. 1		2		3		4	
T, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*, °C.	*P*, mm.
33.0	10.5	51.0	26.2	44.0	17.5	27.0	10.0
41.0	13.0	54.0	31.5	49.9	25.8	32.0	12.2
49.0	21.1	62.0	43.5	51.0	27.1	42.0	14.7
59.5	32.2	76.1	72.2	55.0	32.5	51.0	25.1
70.0	53.5	88.0	116.6	61.4	42.0	61.5	36.0
87.7	106.6	102.6	168.2	69.0	61.0	78.0	71.5
94.6	133.5	114.3	243.6	76.6	80.0	87.0	109.8
106.0	195.0	131.8	384.6	81.0	85.2	105.0	189.1
110.8	227.7	135.0	410.7	88.0	116.6	114.0	251.0
119.0	282.4	145.0	502.6	110.0	218.4	131.9	389.6
130.0	372.2	150.8	604.0	111.4	240.9	135.0	413.6
143.1	514.2	155.5	684.0	133.0	404.4	157.0	696.1
151.2	602.2	158.5	1300.0	156.0	691.0	159.0	1470.0
154.5	697.6						
159.0	1500.0						

TABLE IV

AVERAGE PRESSURES FOR SYSTEMS STUDIED AT TEN DEGREE INTERVALS

Pressure is given in millimeters of mercury at 0°

Systems 1 and 2		System 3		System 5	
T, °C.	*P*, mm.	*T*, °C.	*P*, mm.	*T*, °C.	*P*, mm.
40.0	33.4	130	11.2	30	9.9
50.0	69.8	140	16.2	40	14.1
60.0	109.0	150	24.3	50	24.3
70.0	177.5	160	36.9	60	37.3
80.0	302.3	170	55.9	70	59.7
90.0	450.0	180	78.5	80	85.0
100.0	651.9	190	111.4	90	120.2
110.0	901.5	200	149.8	100	165.4
120.0	1242.0	210	202.5	110	221.4
130.0	1688.0	220	276.9	120	289.6
140.0	2266.0	230	376.1	130	371.2
150.0	2935.0	240	530.7	140	467.2
155.0	3521.0	250	765.9	150	591.9
159.1	3834.0	260	1191.0	155	669.0
		270	1874.0		
		280	3129.0		

Determining the Ratio of Water to Ammonia.—The ratio of water to ammonia in the vapor phase at equilibrium for System 3 was determined at those temperatures at which the dissociation pressures were approximately one atmosphere and one-half an atmosphere. The analysis of the mixtures at these pressures gave the following results.

Discussion of Errors

1. By means of the silver scale and the hair-lined glass which is mounted in a steel frame and slides on a steel rod the manometer may be read to 0.2

TABLE V

THE RATIO OF WATER TO AMMONIA IN THE VAPOR PHASE OF SYSTEM 3 AT EQUILIBRIUM

				At 0° and 760 mm.		Percentage by volume	
	Vol. of gas collected, cc.	Temp., °C.	Total pressure,	Vol. of gas collected, mm.	Vol. of NH_3 by titration, cc.	ammonia, cc.	water vapor
1	52	246	726	28.24	7.82	27.71	72.29
2	52	245	695.8	26.11	6.77	25.95	74.05
3	52	245.3	703.6	25.62	6.65	25.97	74.03
						Av. 26.54	73.46
4	52	229	347.1	12.91	3.45	26.71	73.29
5	52	229	340.9	12.26	3.31	26.59	73.41
6	50	230	340.0	12.17	3.27	26.85	73.15
						Av. 26.72	73.28

The calculated values in the above table were obtained by use of the gas laws uncorrected.

mm. or less. Since most of the pressures read were high, the percentage errors due to this were low. For the lowest readings recorded this is not more than two per cent., while for all readings above 20 mm. it is less than one per cent.

2. The error due to leveling the confining liquid was not more than 0.1 mm., for the two arms of the manometer, very close together, are immediately in front of a bright, metallic millimeter scale.

3. It is impossible to remove all the absorbed air from the system. This is always an error in measuring dissociation pressures by the static method; but, while it cannot be eliminated, it is greatly reduced in this investigation by a more compact apparatus. The surface of the reaction chamber has been decreased to a minimum. The evacuation of the system at least twice at an interval of twelve hours or more before a run was begun aided the removal of adsorbed gases. In System 3, when the tip was broken from the bulb containing the gas which had been generated, all but about one-fourth of one per cent. immediately dissolved in the standard acid.

4. The error due to the vapor pressure of the mercury where it was used as a confining liquid was eliminated by subtracting the vapor pressure of mercury from the total pressures read for the various temperatures.

5. The errors in the measurement of temperature are very small. The electromotive force measurements may be made with a high degree of precision. By means of a curve constructed for this particular thermocouple from the melting points of Bureau of Standards samples of metals, the electromotive force measurements may be very accurately converted to temperatures. The greatest errors in temperature measurements will not exceed 0.1°.

6. The error due to the small changes in the temperature of the furnace is more important. The furnace temperature can be maintained within

0.5°, which corresponds to a maximum error of about 7% in the case of $MgNH_4PO_4 \cdot 6H_2O$ at the lower temperatures where 1° is the equivalent of

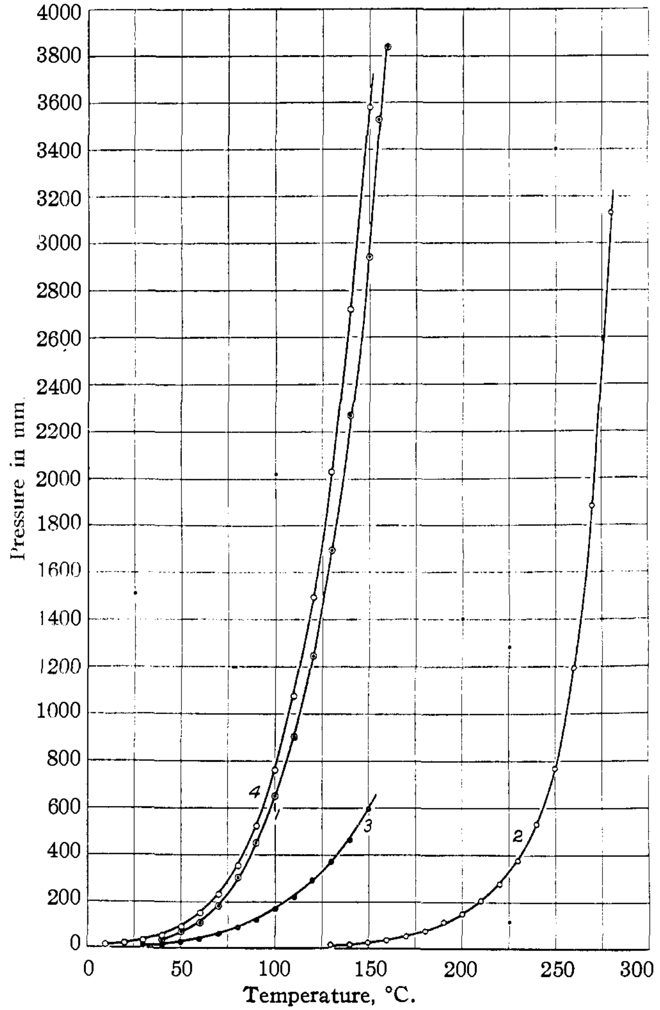

Fig. 2.—The dissociation pressure curves from data in Table IV.

Curve 1. $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O (below 60°) System 1; $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O. NH_3 (above 60°), System 2.

Curve 2. $MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O.

Curve 3. $MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, H_2O; and the aqueous tension curve for the system.

Curve 4. Liquid water, water vapor.

about 7 mm. and the total pressure is about 50 mm. For the exceptionally high dissociation pressures, as of $MgNH_4PO_4 \cdot 6H_2O$ at 150°, a 0.5° error will cause a pressure error of 50 mm., which, however, in a total pressure of 3400 mm., is only one and one-half per cent.

Discussion of Results

The dissociation pressures obtained in this report show that magnesium ammonium phosphate hexahydrate will lose five molecules of water at a very low temperature when heated. Below sixty degrees no ammonia is noticeable in the gaseous phase. The system is univariant and may be expressed by two components. Above sixty degrees, moreover, the ammonium salt has reached an appreciable dissociation which produces another phase while the system still has one degree of freedom. There are consequently two effects, the dissociation of the hexahydrate and the dissociation of the ammonium salt, one superimposed gradually upon the other. Three components are necessary, therefore, to express the system. Data in Table I and Curve 1 in Fig. 2 are the combined results of the systems studied as 1 and 2, both of which are feasibly reversible over the temperature interval investigated. The dissociation pressure of the substance is but slightly below the aqueous tension of water within this temperature range, and it is equal to one atmosphere at 105°. This explains the formation of the monohydrate when magnesium ammonium phosphate is precipitated from boiling solution. The hexahydrate is stable at lower temperatures only. The fact that the dissociation pressure of the hexahydrate reaches a value of 3834 millimeters or over five atmospheres at 159.1° indicates its unstable character.

The dissociation pressures also show that the monohydrate will lose both its water of hydration and its ammonia in an open vessel when it is heated even considerably below 250°, where it reaches the total pressure of one atmosphere. The vapor phase at this temperature consists of approximately three-fourths water vapor and one-fourth ammonia by volume, and equilibrium is quickly established under the prevailing conditions.

In the study of System 3 it was found that in the heating of $MgNH_4PO_4 \cdot H_2O$, magnesium pyrophosphate was formed whenever both water and ammonia were liberated as gases. This indicates that the water vapor pressure due to the loss of water of constitution by magnesium acid phosphate exceeds that due to the loss of water of hydration by magnesium ammonium phosphate monohydrate when both water and ammonia appear in the gaseous phase. Therefore, if $MgHPO_4$ ever should be formed it would dissociate into water and $Mg_2P_2O_7$. Thus another dissociation is gradually superimposed upon both the dissociation of the hydrate and the dissociation of the ammonium salt.

An epitome of the foregoing facts may be given by the following well-known equation, $2MgNH_4PO_4 \cdot 6H_2O \longrightarrow Mg_2P_2O_7 + 13H_2O + 2NH_3$, which summarizes what takes place when the substance is heated to a temperature which need not exceed 250°, in an open vessel where the gases formed escape as liberated. The equilibrium was found to be attained rapidly near 250°. The speed of the reaction therefore when required to proceed in one direction would be sufficiently great to ensure complete expulsion of the volatile substances in a reasonable time.

In System 2 the reaction is quickly and completely reversible up to about 157°, consisting simply of the two hydrates in equilibrium with water vapor. Above 157° the pressure increases in a very rapid and irregular way and the reaction is not feasibly reversible. Pure $MgHPO_4\cdot 3H_2O$ which has been heated in the reaction vessel to 158° or more gives a positive test for pyrophosphate with zinc acetate reagent,[5] while that kept below this temperature shows no trace of it.

In System 3 the reaction is completely reversible, although extremely slow. Pyrophosphate appears at a very low temperature, at 200° or less. Here, however, the pyrophosphate seems to convert back to orthophosphate much more readily than in a similar situation in System 5, whose reversibility was found non-feasible when temperatures were reached where pyrophosphate was formed.

The dissociation of System 4, $MgHPO_4\cdot 7H_2O$, is especially interesting. When freshly prepared, the crystals were exceptionally large and perfectly formed. However, in a day or two, droplets of water appeared on the walls of the glass-stoppered bottle in which the salt was stored. As the long crystals disappeared, the trihydrate, the stable phase, was formed.

It was found, moreover, that the pure heptahydrate, when once inoculated with the trihydrate and evacuated in the pressure–temperature apparatus, formed liquid water in five minutes or less at any temperature from room temperature to at least 100°. The crystals, still in the water from which they were precipitated, left standing on the shelf, also changed completely into the trihydrate at the same temperature at which precipitation took place (about 22°) in about one week. This change, furthermore, was greatly promoted by light. When the pure heptahydrate decomposed, moisture condensed on that side only of the bottle which was turned toward the light. A sample of it, on the other hand, in a glass-stoppered bottle wrapped in a black cloth required a much longer time to change completely into the lower hydrate than an identical unprotected sample standing beside it. It may be concluded, therefore, that magnesium acid phosphate heptahydrate, at room temperature, has a dissociation pressure as great as or greater than the aqueous tension of liquid water.

Summary

1. A modified apparatus is described for measuring the dissociation pressures of substances that give both water and another condensable gaseous substance.

2. A method is given for measuring and for resolving into partial pressures the dissociation pressures of salt hydrates, where both water and

another gaseous substance are produced, and where the total measured pressure may be high.

3. The dissociation pressures for the systems

$MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot H_2O$, H_2O (below 60°)
$MgNH_4PO_4 \cdot 6H_2O$. $MgNH_4PO_4 \cdot H_2O$, $MgHPO_4 \cdot 3H_2O$, H_2O, NH_3 (above 60°)
$MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4$, $Mg_2P_2O_7$, NH_3, H_2O
$MgHPO_4 \cdot 3H_2O$, $MgHPO_4 \cdot H_2O$, H_2O

have been determined.

4. The use of Wood's metal as a confining liquid is described.

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Lead–Mercurous Acetate Voltaic Cell with Acetic Acid as the Solvent[1]

BY GRADY TARBUTTON AND WARREN C. VOSBURGH

The reproducibility that has been attained in the preparation of voltaic cells with non-aqueous electrolytes is in general less than that of cells with aqueous electrolytes. Among those who have attained a reproducibility of within a few tenths of a millivolt are Brodsky,[2] Afanasiew,[3] Isaacs and Partington,[4] and Harned and Fleysher,[5] all with alcoholic electrolytes, and Yoshida,[6] who set up cadmium–mercurous iodide cells with water, methanol, ethanol, propanol and acetone as solvents. The electromotive forces in most other investigations with non-aqueous electrolytes have been reported only to the nearest millivolt.

It seemed worth while to test the reproducibility of cells with acetic acid as the electrolyte solvent. Hutchison and Chandlee[7] have prepared a series of hydrogen–mercurous sulfate cells with acetic acid as the solvent, but the difficulty of either excluding water entirely or keeping its concentration very constant was involved. The cell chosen for this work was a lead–mercurous acetate cell, which when pure acetic acid is the solvent can be represented as follows

$$Pb(Hg) \mid Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2 \mid Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2, Hg_2(C_2H_3O_2)_2 \mid Hg$$

Materials and Apparatus.—The purification of the acetic acid and of the lead acetate are described in an earlier paper.[8] Mercurous acetate was

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[1] Part of a thesis submitted by Grady Tarbutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, 1932.

[2] Brodsky, *Z. physik. Chem.*, **121**, 9 (1926).

[3] Afanasiew, *Z. Elektrochem.*, **35**, 221 (1929).

[4] Isaacs and Partington, *Trans. Faraday Soc.*, **25**, 56 (1929).

[5] Harned and Fleysher, THIS JOURNAL, **47**, 82 (1925).

[6] Yoshida, *Chem. Abs.*, **22**, 1893 (1928).

[7] Hutchison and Chandlee, THIS JOURNAL, **53**, 2884 (1931).

[8] Tarbutton and Vosburgh, *ibid.*, **54**, 4537 (1932).