# THE JOURNAL

## OF THE

# American Chemical Society
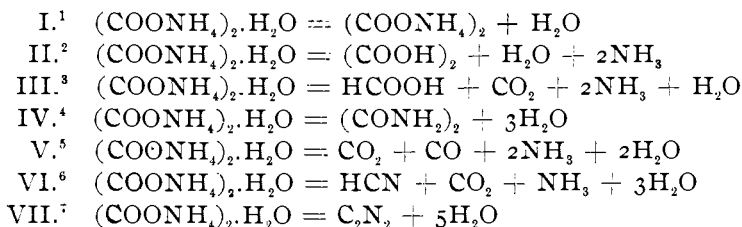
## DECOMPOSITION OF HYDRATED AMMONIUM SALTS.

BY WILLIAM M. DEHN AND EDWARD O. HEUSE.
Received May 31, 1907.

Under the influence of rising temperatures, diammonium oxalate[1] decomposes as follows:

$$\text{I.}^1 \quad (COONH_4)_2.H_2O = (COONH_4)_2 + H_2O$$
$$\text{II.}^2 \quad (COONH_4)_2.H_2O = (COOH)_2 + H_2O + 2NH_3$$
$$\text{III.}^3 \quad (COONH_4)_2.H_2O = HCOOH + CO_2 + 2NH_3 + H_2O$$
$$\text{IV.}^4 \quad (COONH_4)_2.H_2O = (CONH_2)_2 + 3H_2O$$
$$\text{V.}^5 \quad (COONH_4)_2.H_2O = CO_2 + CO + 2NH_3 + 2H_2O$$
$$\text{VI.}^6 \quad (COONH_4)_2.H_2O = HCN + CO_2 + NH_3 + 3H_2O$$
$$\text{VII.}^7 \quad (COONH_4)_2.H_2O = C_2N_2 + 5H_2O$$

Some of these reactions take place at approximately the same temperatures; others only at successively higher temperatures. That equation I represents the initial decomposition is established with certainty[1]; the end-products at high temperature are shown to be largely cyanogen and water. It w ᴐ e observed that only equations I and II represent reversible reactions which are rapid and complete; the products of reaction III condense to ammonium formate and ammonium bicarbonate; some of the products of reaction V and VI condense to ammonium carbonate and ammonium bicarbonate; reaction IV and VII[8] are practically non-reversible.

[1] Dupre, Analyst, 30, 266; Ber., 18, 1394; Gillot, Bull. Acad. Roy. Belg., 1900, 744.
[2] Gillot; Gay Lussac, Ann. chim. phys., 46, 218.
[3] Turner. Schweigg, Jour. 62, 444; Pogg. Ann., 24, 166. Dumas, Ann. chim. phys., 44, 129 (1830).
[4] Ibid, 54. 240.
[5] Dumas; Gay Lussac; Lorin, Compt. rend., 82, 750.
[6] Dumas.
[7] Dumas; Michael, Ber. 28, 1632.
[8] Peleuse and Richardson (Ann. 26, 63) show that water and cyanogen yield ammonium oxalate. Zellet (Monatshefte 14, 224) finds that when cyanogen is heated with water at 100°, he obtains oxalic, hydrocyanic and azulmic acids, urea, carbon dioxide, and ammonia.

From consideration not only of the number of these possible reactions but also of the diversity of the products formed, it may be supposed that the decomposition of this simple salt involves a hopeless complexity; however, the following studies seem to indicate that the order of successive decompositions is largely as shown in the equations:

$$(COONH_4)_2.H_2O = (COONH_4)_2 + H_2O$$
$$(COONH_4)_2 = (CONH_2)_2 + 2H_2O$$
$$(CONH_2)_2 = C_2N_2 + 2H_2O$$
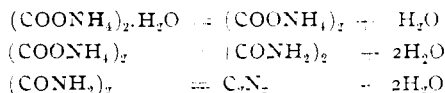
Samples of pure diammonium oxalate in open crucibles were heated in air baths whose temperatures were held constant during one hour. The total loss in weight and the residual ammonia were determined in each experiment with the following results:

| | | Loss per cent of | | |
| --- | --- | --- | --- | --- |
| Experiment | Temperature | Total | Ammonia | Water[1] |
| I | 80° | 9.51 | .... | 9.51 |
| 2 | 95° | 12.17 | .... | 12.17 |
| 3 | 118° | 13.17 | .... | 13.17 |
| 4 | 143° | 14.02 | .... | 14.02 |
| 5 | 153° | 15.42 | 0.33 | 15.09 |
| 6 | 168° | 63.78 | 6.75 | 56.03 |
| 7 | 178° | 78.65 | 13.86 | 64.73 |
| 8 | 193° | 87.89 | 13.92 | 74.03 |
| 9 | 245° | 89.21 | 18.95 | 70.26 |

These experiments show that when dry diammonium oxalate is heated:

1. It evolves one molecule of water below 100°[2] (Equation 1); and, to 150° at least, decomposes according to Equation IV.

2. Below 168° the loss of water is even greater than that represented by equation IV (38.02 per cent.); hence oxamide is largely formed at these temperatures.

3. At 150° ammonia begins[3] to be evolved (Equation II) and at higher temperatures it continues to be evolved or else the substance sublimes.

Since oxamide sublimes but, as shown below, does not decompose into cyanogen and water (Equation VII) below 280°, it may be concluded that the lower temperatures represent only two main decompositions (I and IV). Efforts were made to confirm this by vapor pressure curves.

[1] And other products at higher temperature; the total per cent. of water is 63.37 per cent.

[2] One molecule of water represents 12.67 per cent.

[3] Gillot (*J. Chem. Soc.*, 1901, A 118) shows that ammonia is completely hydrolyzed and expelled from boiling solutions of diammonium oxalate.

### VAPOR PRESSURES OF DIAMMONIUM OXALATE.

| Temp. | Pressure | Temp. | Pressure |
|---|---|---|---|
| 71 | 11 | 145 | 2134 |
| 74 | 19 | 156 | 2748 |
| 82 | 53 | 161 | 3144 |
| 85 | 58 | 168 | 3877 |
| 90 | 72 | 171 | 4319 |
| 95 | 78 | 176 | 4821 |
| 98 | 85 | 180 | 5233 |
| 111 | 314 | 182 | 5546 |
| 121 | 597 | 187 | 6084 |
| 122 | 827 | 195 | 7103 |
| 126 | 999 | 197 | 7326 |
| 131 | 1271 | 200 | 7682 |
| 138 | 1616 | 205 | 8219 |
| 141 | 1815 | 210 | 8818 |

### VAPOR PRESSURES OF OXAMIDE.

| Temp. | Pressure | Temp. | Pressure |
|---|---|---|---|
| 265[1] | 45 | 293 | 1596 |
| 270 | 71 | 294 | 1911 |
| 274 | 86 | 294.5 | 2115 |
| 277 | 118 | 295 | 2157 |
| 283 | 241 | 295.5 | 2301 |
| 290 | 278 | 296.5 | 2412 |
| 291 | 1182 | 297 | 2536 |
| 292 | 1383 | 297.5 | 2752[2] |

It will be observed that the vapor pressure curve of diammonium oxalate is represented by three distinct segments. Segment A unquestionably represents the partial aqueous decomposition; segment B evidently represents the elimination of the molecule of water of crystallization (equation I); and segment C represents the decomposition into oxamide and probably the simultaneous decomposition represented by equation II, III, V and VI. That reaction VII does not take place below 290° is sufficiently indicated by the curve of oxamide.

### Monoammonium Oxalate.

This salt, prepared by the methods of Nichols[3] and Walden[4], was found to be pure $NH_4HC_2H_4.H_2O$. It is reported that when heated, this salt is stable to 70° ; at higher temperatures, it begins to lose its water of crystallization[5]; at 140° it forms oxamic acid[6]; at more elevated temperatures, it yields carbon dioxide, carbon monoxide, formic acid and oxamide ; finally, it expels hydrocyanic acid and ammonium carbonate; the residue contains oxamic acid and oximide .

When samples of the salt were heated in open crucibles in the manner indicated above, the following data were obtained:

[1] Sublimation was observed at this temperature.

[2] The non-reversible pressure was equal to 1182 mm.; a large quantity of cyanogen was found.
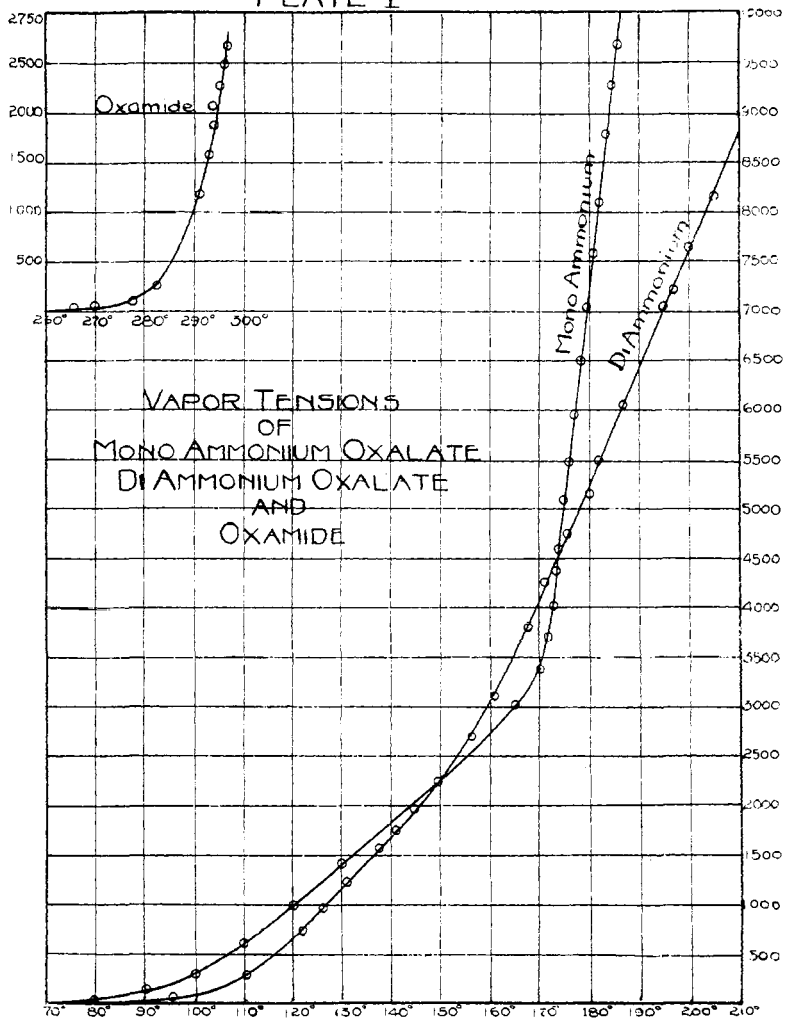
[3] Chem. News, 22, 14.

[4] Am. Ch. J., 34, 147.

[5] Balard, Ann. chim. phys., (3) 4, 94; Ann., 42, 197.
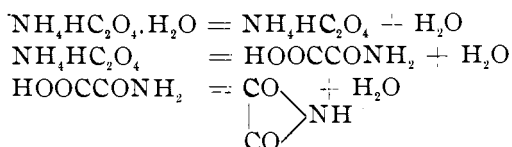
[6] Ost. and Mente, Ber., 19, 3229.

## PLATE I



VAPOR TENSIONS
OF
MONO AMMONIUM OXALATE
DI AMMONIUM OXALATE
AND
OXAMIDE

| Experiment | Temperature | Loss per cent. of | | |
| --- | --- | --- | --- | --- |
| | | Total | Ammonia | Water |
| 1 | 75 | . . . | . . . | . . . |
| 2 | 94 | 2.68 | . . . | 2.68 |
| 3 | 105 | 7.47 | . . . | 7.47 |
| 4 | 115 | 8.54 | . . . | 8.54 |
| 5 | 134 | 9.09 | 0.13 | 8.96 |
| 6 | 155 | 10.99 | 0.30 | 10.69 |
| 7 | 169 | 11.51 | 1.03 | 11.48 |
| 8 | 183 | 48.36 | 1.71 | 46.65 |
| 9 | 200 | 88.51 | 8.98 | 79.53 |
| 10 | 225 | 99.64 | 12.24 | 87.40 |

It is seen that monoammonium oxalate:

1. Is stable to $75°$,

2. Parts with its molecule of water of crystallization (14.40 per cent.) below $170°$.

3. Loses two other molecules of water at $183°$ and simultaneously incurs a secondary decomposition or *sublimes*.

Therefore the main successive decompositions are probably indicated by the equations:

$$NH_4HC_2O_4 \cdot H_2O = NH_4HC_2O_4 + H_2O$$
$$NH_4HC_2O_4 \quad = HOOCCONH_2 + H_2O$$
$$HOOCCONH_2 = \begin{matrix} CO \\ | \\ CO \end{matrix} \!\!\!\! \rangle NH + H_2O$$

The above data of decomposition are closely confirmed by the vapor pressures of the substance.

| Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|
| 81 | 7.7 | 145 | 2131 |
| 88 | 15.9 | 150 | 2370 |
| 95.8 | 50.2 | 155 | 2682 |
| 106 | 469 | 160 | 2964 |
| 110 | 686 | 165 | 3096 |
| 115 | 875 | 170 | 3268 |
| 122 | 1102 | 175 | 4009 |
| 125 | 1230 | 176 | 5862 |
| 130 | 1420 | 180 | 7427 |
| 135 | 1623 | 182 | 8159 |
| 140 | 1840 | 185 | 9846 |

It will be observed (see plate 1) that (1) the general form of the two curves are much alike, (2) the molecule of water in each salt is completely eliminated below $100$-$170°$, and (3) the upper segments represent the second stages of decomposition.

Decompositions of the above organic compounds indicate that the initial and predominating reactions involve the expulsion of water; and that simultaneously, particularly at higher temperatures, secondary reactions indicated by the dissociation of ammonia, are involved. It was hoped that studies of inorganic hydrated ammonium salts, along the lines indicated above, would lead to a more intimate knowledge of water of crystallization and of the structure of hydrated salts. That this hope has been partially realized is evidenced by the following studies.

It was found, for instance, that certain hydrated ammonium salts decompose so as to yield both water and ammonia at most temperatures above the initial temperature of decomposition. Studies of the *rate* of expulsion of water and ammonia have shown that abundant yields of ammonia usually accompany the largest yields of water; and, though the last trace of ammonia is given off only with the last trace of water, it is given off simultaneously with it at most of the lower temperatures. In

other words, curves of expulsion of ammonia, as well as of water, extend from the temperatures of initial decomposition to those of complete decomposition; consequently tracing the course of ammonia through the *composite* decompositions leads to knowledge of the respective individual decompositions and, as will be shown, throws light upon individual structures in the complete structure. For instance, suppose it can be shown that highly polyhydrated ammonium salts are largely decomposed below 100°, while the residues of ammonia and of "water of composition" are completely expelled only at considerably higher temperatures, it may then be concluded that *the union of ammonia resembles more closely the union of "water of composition" than the union of "water of crystallization."* Again suppose it can be shown that ammonia is given off at all lower temperatures, it may also be concluded that *both "water of crystallization" and "water of composition" are given off at all of these lower temperatures.*

In respect to the methods used to differentiate the respective dissociations, it has been found that vapor pressure curves (*vide plate VII*) are not necessarily indicative of the *qualitative* decompositions of compounds; in the case of polyhydrated salts they are a measurement only of the *composite* effect of a number of co-temporaneous dissociations. For instance if each molecule of water and ammonia in the original compound has a definite vapor pressure for each temperature, it may easily be seen that the resultants of their pressures may so blend as to indicate no definite breaks in the vapor pressure curve, therefore, *recognition of points of decomposition may fail entirely when only vapor pressure curves are studied.* For this reason other methods of investigation have been employed.

### Decomposition of Inorganic Salts.

Various investigators[1] have represented partially dehydrated salts, for instance, hydrated ammonium salts, by very contradictory and, as shown below, by very erroneous formulas. We find in the periodicals and the text-books that free use is made of formulas:

$$(NH_4MgAsO_4)_2.H_2O \text{ and } (NH_4MgPO_4)_2.H_2O$$
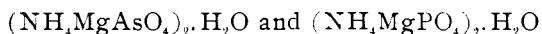
to represent ammonium magnesium arsenate and ammonium magnesium phosphate dehydrated at 100-110°: Though most investigators agree that the composition of ammonium magnesium arsenate at ordinary temperature is $NH_4MgAsO_4 6H_2O$, a considerable difference of opinion as to its composition at temperatures between 98° and 100° is expressed. For instance Bunsen[2] concludes that nearly ½ of a molecule of water is held at 98°. Rose[3], Puller[4], Field[5], and Lefevre[6], affirm that exactly ½ mol. $H_2O$ is retained

[1] Wach, Schweigger's J. Chem. Physik, 59, 288; Rose, Z. anal. Chem., 1, 417; Ann. Physik., 76, 20; Z. anorg. Chem., 23, 146. Puller, Z. anal. Chem., 10, 68.
[2] Ann. Pharm., 192, 311.
[3] Z. anal. Chem., 1, 417.
[4] Ibid, 10, 68.
[5] Jahrsb., 1858. 170.
[6] Ann. chim. phys., (6) 27, 55.

by the salt when it is dried at 100° on the water bath ; Fuller holds that it is practically dehydrated at 103° ; and Bunsen[1] further states that is completely dehydrated at 104.5°.   These data do not appear to be particularly discordant ; but in view of the fact, as shown in this research, that 3-4 per cent. of ammonia—equivalent in weight to about $\frac{1}{2}$ mol. $H_2O$—are lost at these temperatures, none of the conclusions drawn are correct. For when the salt is dried at these temperatures less ammonia and more water are present than are represented by the formula $(NH_4MgAsO_4)_2$.-$H_2O$.   A more correct representation would be a mixture in equal proportions of $HMgAsO_4.H_2O$ and $NH_4MgAsO_4.H_2O$.   However, even this formulation will be shown to be incorrect, for one conclusion of these studies is that *no definite formula can be given to many hydrated ammonium salts dried at temperatures between 40°-200°*.

This is clearly illustrated by data obtained on heating samples of these salts at definite intervals of temperature for equal lengths of time and determining both the total loss in weight sustained and also the weight of ammonia evolved.   The salts, contained and weighed in U-shaped tubes, were heated in baths controlled by thermostats, while air, dried and freed from carbon dioxide, was passed continuously through the tubes and into flasks containing standard sulphuric acid.   The total loss of weight in the U-tubes represented, of course, the loss of both water and ammonia ; this weight, less than the weight of ammonia, determined by titration, gave the loss of water.

It was found that quite different results were obtained when we varied the following conditions :   1. Temperature.   2. Time.   3. Kind of drying gas.   4. Quantity of drying gas.   5. Size of salt crystals.   6. Preservation of salt crystals.   7. Manner of heating.

The effect of temperature is the most important and it was on temperature as a basis that the following studies were made.

The influence of time was soon found to be a very disturbing factor, for these salts do not dry to definite composition, therefore briefer or longer desiccation gave very widely different per cents. of decomposition. This is seen in the following table :

| Substance | Weight | Loss | Loss per cent. | Time | Temp. |
|---|---|---|---|---|---|
| $NH_4MgPO_4.6H_2O$ | 0.7473 | 0.0423 | 5.66 | 4 | 70° |
| $NH_4MgPO_4.6H_2O$ | 0.4636 | 0.1658 | 35.76 | 40 | 70° |
| $HNaNH_4PO_4.4H_2O$ | 0.8016 | 0.1178 | 14.70 | 4 | 76° |
| $HNaNH_4PO_4.4H_2O$ | 4.7094 | 1.0784 | 22.89 | 57 | 75° |
| $NH_4MgAsO_4.6H_2O$ | 0.7941 | 0.0136 | 0.35 | 4 | 50° |
| $NH_4MgAsO_4.6H_2O$ | 0.7958 | 0.0372 | 4.67 | 20 | 50° |
| $NH_4MgAsO_4.6H_2O$ | 0.2920 | 0.1108 | 37.95 | 4 | 110° |
| $NH_4MgAsO_4.6H_2O$ | 1.1127 | 0.4556 | 39.61 | 40 | 110° |

It will be observed here that heating for four hours invariably gave lower per cents. of decomposition than when heating for 20-57 hours.   An ex-

[1] loc. cit.

planation of these great differences of results on short and protracted heating is conceivable when one recalls that "water of crystallization" is more easily expelled than "water of composition". The former is usually eliminated at temperatures below 100°; the latter, at temperatures above 100°. By protracted heating at low temperatures, however, "water of composition" may be removed completely, therefore too prolonged heating at low temperature does not reveal the normal decomposition at these temperatures. On the other hand too brief a heating at low temperatures does not insure complete removal of the decomposition products. It was to avoid on the one hand incomplete dehydration, and on the other excessive secondary decomposition that periods of 4–7 hours heating were finally chosen.

It was found, moreover, that heating the salts progressively, that is heating the same sample to successively higher temperatures, did not yield the proper results, for, on comparing the per cents. of decomposition obtained by heating different samples at the respective temperatures, very different results were obtained.

The method of heating individual samples at different temperatures for the same lengths of time was adopted, in preference to heating the same sample successively to higher temperatures, for the reason that the former method really eliminates the element of time and thus minimizes secondary decompositions. For instance when a sample of a salt is heated at 65° for four hours and then another sample of the same salt is heated at 70° for four hours, all other conditions remaining the same, the difference of effect is the result of temperature alone. A further reason for employing the method of separate samples for each interval of temperature, was to avoid the accumulative errors of analysis involved in the other method.

The effect of using different gases to carry off the decomposition products may be seen in the use of hydrogen and of air. In the following table, the data were obtained on heating microcosmic salt for periods of four hours each.

| Temperature | Per cent. | Carrier |
|---|---|---|
| 50° | 0.35 | Hydrogen |
| 50° | 0.60 | Air |
| 50° | 0.59 | Air |
| 76° | 9.64 | Hydrogen |
| 75° | 16.35 | Air |

The results here indicate that hydrogen is not so efficient a carrier as air, and this undoubtedly is owing to the fact that it possesses a much more rapid rate of diffusion.

The effect of *speed*, or rather the quantity, of carrying gas, is seen in the following experiment. Dry air was passed for 27 hours over 4.4334 grams of $NH_4MgAsO_4.6H_2O$; it lost 0.2114 grams or 4.89 per cent.

whereas another sample of 3.4729 grams exposed to quiet air for the same time lost scarcely a weighable quantity.

The air used in the following experiments was regulated so that 60–70 bubbles per minute passed from the exit-tube dipping into the flasks containing the standard acid. At first considerable difficulty was encountered in regulating this passage of air but after a number of trials the following, quite satisfactory system was adopted. The air from the main supply was passed through a bottle connected on the one hand with the drying-train and on the other with a shunt tube dipping into a definite depth of water. The object of the shunt was to force through the drying system air backed by a constant pressure, equal always to the height of water in the shunt system when air was constantly passing out of the latter. The quantity of air passing through the drying system was controlled by a screw clamp attached to a rubber tube in connection with the exit tube. By this means the number of bubbles per minute could be regulated to a nicety; the size of the bubbles passing through the normal sulphuric acid, was limited, of course, by the size of the exit tube dipping into it.

Fifthly, the size of the salt crystals used was found to exercise a very appreciable effect on the results; mass varying as the cube, and radiating surfaces as the square of the diameter. To reduce this influence to a minimum the crystals were pulverized so as to pass through a particular, fine-mesh sieve.

Sixthly, efflorescence of some salts, for instance with ammonium calcium arsenate, was found to introduce large factors of error. The weathering, that is the decomposition of these salts at ordinary temperature, is often so great, particularly in summer, that only freshly prepared samples could be used.

Finally, the manner of heating, for instance, whether in open crucible, in desiccators over sulphuric acid, or in the U tubes mentioned above, was found to yield different per cents. of decomposition. Of course the same method of heating was employed throughout any given experiment, nevertheless at some temperatures certain abnormal results were often obtained and can be explained only on the basis of "suspended transformation". For instance in the following table:

| Substance | Temperature | Per cent. volatilized |
|---|---|---|
| $Al_2(SO_4)_3.18H_2O$ | 83.0 | 11.79 |
| " | 90.5 | 4.69 |
| $K Al(SO_4)_2.12H_2O$ | 71.5 | 8.35 |
| " | 83.0 | 2.21 |

it is seen that higher temperatures yield lower per cents. of decomposition though the experiments were carried out under similar conditions. Heating *at once* to the higher temperatures seems to induce this "suspended transformation." [1]

[1] See page 1161.

Though recognizing the above mentioned influences and observing in the experiments every precaution necessary to avoid their disturbing effects, concordant results were often obtained only after repeated trials. This difficulty of obtaining concordant results was particularly noticeable at temperatures at which more than one molecule of water was given off, for instance in the case of ammonium magnesium arsenate, at 70–90°.

The following table includes data obtained in studying the decomposition of ammonium magnesium arsenate prepared in the usual manner and found by analysis to be strictly $NH_4MgAsO_4.6H_2O$.
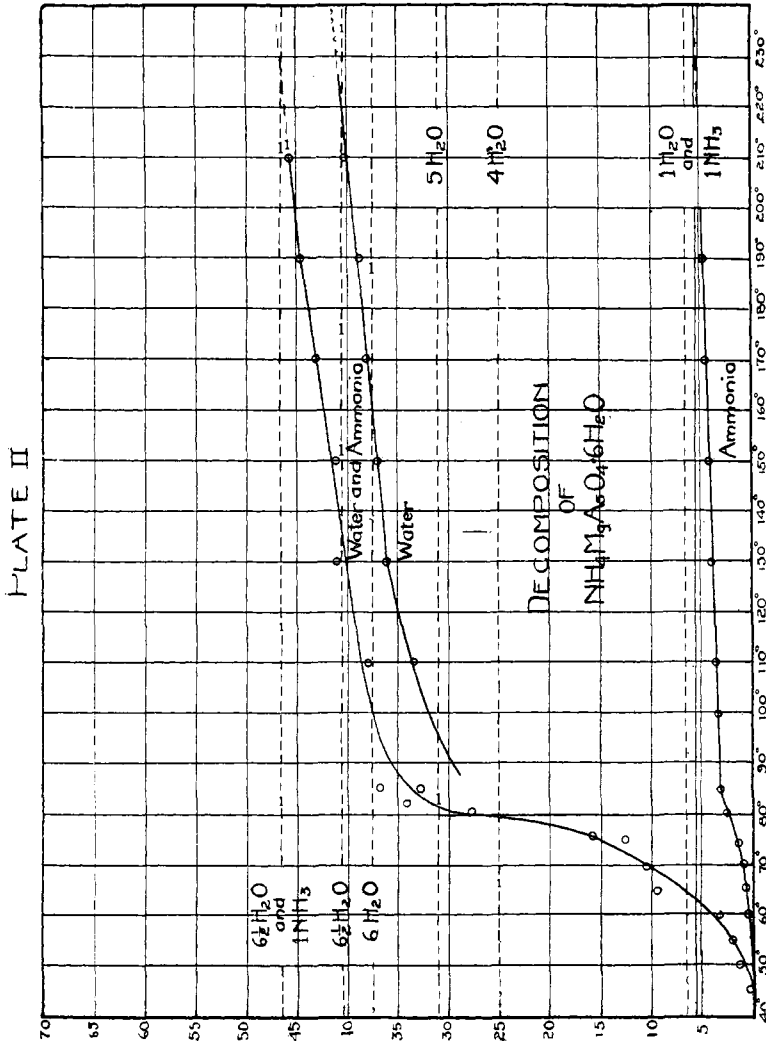
| I Temperature | II Weight salt | III Loss of weight of $H_2O+NH_3$ | IV $NH_3$ | V $H_2O$ | VI Ratio of Both | VII $H_2O+NH_3$ | VIII Total per cent. loss of $NH_3$ | IX $H_2O$ | X $H_2O+NH_3$ | XI Fractional per loss of $NH_3$ | XII[1] cent. $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 0.7752 | .0008 | .0002 | .0006 | 4.0 | 0.10 | 0.02 | 0.08 | 0.10 | 0.02 | 0.08 |
| 45 | 1.0344 | .0030 | .0003 | .0027 | 9.0 | 0.29 | 0.03 | 0.26 | 0.19 | 0.01 | 0.18 |
| 50 | 0.2692 | .0042 | .0003 | .0039 | 13.0 | 1.56 | 0.11 | 1.45 | 1.27 | 0.08 | 1.19 |
| 56 | 0.2875 | .0053 | .0005 | .0053 | 10.6 | 2.01 | 0.17 | 1.84 | 0.45 | 0.07 | 0.38 |
| 60 | 0.6945 | .0264 | .0027 | .0237 | 8.8 | 3.80 | 0.39 | 3.41 | 1.79 | 0.22 | 1.57 |
| 65 | 0.6482 | .0629 | .0063 | .0566 | 8.9 | 9.70 | 0.97 | 8.73 | 5.90 | 0.58 | 5.32 |
| 70 | 0.8108 | .0828 | .0093 | .0735 | 8.0 | 10.21 | 1.15 | 9.06 | 0.51 | 0.18 | 0.33 |
| 75 | 0.2698 | .0343 | .0039 | .0304 | 7.8 | 12.71 | 1.34 | 11.57 | 2.50 | 0.19 | 2.31 |
| 75 | 0.2332 | .0379 | .0038 | .0341 | 8.9 | 16.55 | 1.72 | 14.65 | 3.64 | 0.38 | 3.26 |
| 80 | 0.5166 | .1563 | .0164 | .1399 | 8.5 | 30.26 | 3.18 | 27.08 | 13.91 | 1.46 | 12 45 |
| 82 | 0.2402 | .0832 | .0087 | .0745 | 8.5 | 34.64 | 3.63 | 31.01 | 4.38 | 0.45 | 3.93 |
| 85 | 0.5164 | .1162 | .0122 | .1140 | 8.5 | 36.72 | 3.86 | 32.86 | 2.08 | 0.13 | 1.95 |
| 100 | 0.3247 | .1212 | .0127 | .1085 | 8.6 | 57.31 | 3.90 | 33.41 | 0.59 | 0.04 | 0.55 |
| 110 | 0.2920 | .1108 | .0116 | .0992 | 8.6 | 37.95 | 3.97 | 33.98 | 0.64 | 0.07 | 0.57 |
| 130 | 0.0708 | .0288 | .0030 | .0258 | 8.6 | 40.68 | 4.24 | 36.44 | 2.75 | 0.27 | 2.46 |
| 150 | 0.1156 | .0478 | .0050 | .0428 | 8.5 | 41.35 | 4.32 | 37.03 | 0.67 | 0.08 | 0.59 |
| 170 | 0.1478 | .0638 | .0072 | .0566 | 8.0 | 43.17 | 4.86 | 38.31 | 1.82 | 0.54 | 1.28 |
| 190 | 0.2496 | .1106 | .0128 | .0978 | 7.6 | 44.32 | 5.12 | 39.20 | 1.15 | 0.26 | 0.89 |
| 210 | 0.3641 | .1670 | .0196 | .1474 | 7.5 | 45.86 | 5.40 | 40.46 | 1.54 | 0.28 | 1.26 |
| 225 | 0.6541 | .3035 | .0384 | .2651 | 6.9 | 46.40 | 5.90 | 40.50 | 0.54 | 0.50 | 0.04 |

When $NH_4MgAsO_4.6H_2O$ is heated it may sustain any of the following losses or their intermediate per cents.:

| Loss of Molecules of | Per cent. of loss |
|---|---|
| $NH_3$ | 5.88 |
| $H_2O$ | 6.23 |
| $2H_2O$ | 12.46 |
| $3H_2O$ | 18.69 |
| $4H_2O$ | 24.92 |
| $5H_2O$ | 31.15 |
| $6H_2O$ | 37.37 |
| $6\frac{1}{2}H_2O$ | 40.49 |
| $6\frac{1}{2}H_2O - NH_3$ | 46.37 |

The above experimental data plotted with per cents. as ordinates and degrees of temperature as abscissas, give from columns VIII, IX and VII respectively, the curves of evolution of ammonia, water, and both ammonia and water.

[1] These fractional per cents. are obtained by subtracting adjacent total per cents.; they indicate the effect of the *increment* of temperature.

PLATE II

DECOMPOSITION OF NH₄MgAsO₄.6H₂O

Water and Ammonia

Water

Ammonia

$6\frac{1}{2}H_2O$ and $1NH_3$

$6\frac{1}{2}H_2O$

$6H_2O$

$5H_2O$

$4H_2O$

$1H_2O$ and $1NH_3$

It will be observed that:

1.  Both water and ammonia begin to be given off at 40° and are completely removed at 225°.

2.  Fully one-half of all the ammonia is expelled below 80°, the remainder, between temperatures 85-225°.

3.  About the *same ratios*[1] of water and ammonia are given off at temperatures 60-210°[2].

[1] Between 60-150° the ratio of weight of water to ammonia averages 8.5 : 1, which is equal to a molecular ratio of 8.0 : 1.    The mass ratio of water to ammonia in $NH_4MgAsO_4$ is 6.9 : 1.    In determining the data for the above table, wide variations from the ratio of 8.5 : 1 always indicated experimental errors.

[2] See column VI above.    This approximate constancy of ratio is not in evidence with other salts (see $NH_4MgPO_4.6H_2O$) except at high temperatures.

4.   Water is gradually given off below 65°.

5.   Then below 80° the remainder of *four* molecules of water is given off[1].

6.   The *next two* molecules are given off at temperatures between 80-150°.

7.   The *last one-half molecule* of water, derived from the ammonium-oxygen group $(NH_4O-)$, is slowly expelled at temperatures 150-225°; at the last of these temperatures, magnesium pyroarsenate is formed.

The fact that two molecules of water are given off, finally and independently of each other, and of the other four molecules is confirmed by the following experiment.   The salt containing the six molecules of water was heated for three hours on the water-bath in closed vessels with a large quantity of ordinary alcohol.   After cooling, washing by decantation, first with alcohol, then with ether, and finally drying for a short time in a vacuum dessicator, it was found that dehydration and removal of ammonia from the salt had resulted.

This is shown in the following analyses :

|  | Per cent. loss |
|---|---|
| 0.5541 grams substances gave 0.2035 grams $Mg_2As_2O_7$ $\equiv$ ........... | 25.59 |
| 0.4111 grams substances gave 0.3058 grams $Mg_2As_2O_7$ ............ | 25.63 |
| Average ............. | 25.61 |

|  | Per cent. $NH_3$ |
|---|---|
| 0.0738 grams substances gave 0.0021 grams $NH_3$................. | 2.85 |
| 0.0524 grams substances gave 0.0015 grams $NH_3$................. | 2.92 |
| Average ................. | 2.88 |

Now the total loss by ignition less the ammonia is equal to the water , $25.61 - 2.88 = 22.74$ per cent. $H_2O$.   Theory $2HMgAsO_4.2H_2O = 22.50$ per cent. $H_2O$.   Therefore, after dehydrating $NH_4MgAsO_4.6H_2O$ by means of ordinary alcohol, two molecules of water remain, so they must be different from the other four molecules.

This difference of the last two molecules of water from the other four molecules evidently must involve a difference in structure, that is, there must exist for these water molecules different forms of union in the parent molecule.   If it is tenable that such *differences of coherence of molecules of water involves differences of structure*, then conversely it may be held that *molecules simultaneously expelled involve similarity of structures*. Now since it is true, as was shown above, that $NH_4MgAsO_4.6H_2O$ possesses two molecules of water differing from one another and from the
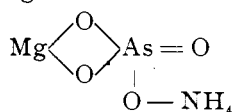
[1] It may appear from the curve of evolution of water that *five* and not *four* molecules of water are expelled simultaneously; but it must be remembered that each of the six molecules of water contributes at all lower temperatures its quota, consequently at the decomposition point for four molecules, a surplus derived from the other two and a half molecules will be obtained.   The alcohol-dehydrating method establishes beyond a doubt the dissimilarity of four molecules of water, (water of crystallization) from the remainder of water (water of composition).

other four—it is interesting to see what structures will account for all of the facts.
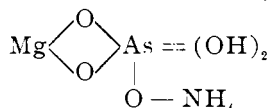
In the first place there can be little doubt that water of crystallization is held in definite molecular structures, and that the structural formula of arsenic acid is :

$$(HO)_3 \equiv As = O$$

and that its ammonium magnesium salt is :

$$Mg \begin{matrix} \diagup O \diagdown \\ \diagdown O \diagup \end{matrix} As = O$$
$$\underset{O - NH_4}{|}$$

and its salt containing one molecule of water (water of composition) is :

$$Mg \begin{matrix} \diagup O \diagdown \\ \diagdown O \diagup \end{matrix} As = (OH)_2$$
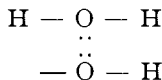$$\underset{O - NH_4}{|}$$

This last structure accounts for the fact that one molecule of water is given off finally and with more difficulty than the other five molecules of water. The fact that the last two molecules of water differ from the other four molecules and differ from each other may be accounted for by the following structure :
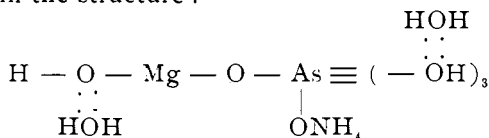
$$H - O - Mg - O - As \equiv (OH)_3$$
$$\underset{O - NH_4}{|}$$
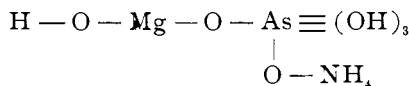
from which on heating one molecule of water would certainly be more easily expelled than the other.[1]

Now since there are four hydroxyls in this structure, they can offer similar points of attachment for four molecules of water (of crystallization), as may be seen individually in the structure :

$$H - \overset{..}{O} - H$$
$$- \overset{..}{O} - H$$

and completely in the structure :

$$H - \underset{\overset{..}{H}\overset{..}{O}H}{O} - Mg - O - As \equiv (- \overset{..}{\overset{..}{O}}H)_3$$

$$\underset{ONH_4}{\overset{HOH}{}}$$

[1] Though no data of the relative stabilities of $H_3AsO_4$ and $Mg(OH)_2$ toward heat are available, it may be inferred, since the former shows greater tendency than the latter to add water, that the hydroxyl attached to magnesium is more easily expelled than the hydroxyl attached to arsenic. However, this point is not so important, here, as the establishment of the structure $H - O - Mg - O - As$. It seems reasonable to hold that the above condition of magnesium is more probable than as shown in $Mg \begin{matrix} \diagup O \diagdown \\ \diagdown O \diagup \end{matrix} As$. At any rate the above structure affords the necessary number of points of attachment for all of the water of crystallization and accounts for the constitution of hydrated ammonium magnesium arsenate and other salts.

This molecular aggregate could split off four molecules of water at or near the same temperature; at a higher temperature, one other molecule of water; and finally and with difficulty the last molecule (and a half) of water.

It may be held that the molecule of water attached to the oxygen in H—O—Mg differs from the three attached to the oxygen in —As—O—H and consequently could involve a difference in coherence in the parent molecule.   That *this molecule actually differs* is shown by the data given on page 1161.

It is observed (see plate VI) that one molecule of water is dissociated below 35°, hence all of the facts are in harmony with the above structure.

It may be contented that ammonia does not cohere in the manner indicated by the structure — O — NH₄ but rather in the manner shown in the structure — O — H.   Either mode of union is in harmony with

$$\overset{\cdot\,\cdot}{N}H_3$$

the main structure of ammonium magnesium arsenate as shown above, but the latter of these two perhaps more readily accounts for the ease with which ammonia is expelled at moderate temperatures simultaneously with the water of crystallization.   However, it does not explain the fact that the last portions of ammonia are expelled with difficulty and long after all of the "water of crystallization" has retired; nor does it explain the fact that different salts containing the same mass of crystal water manifest varied degrees of coherence for ammonia.   These conditions can be explained only on the basis of *composition* of the remainder of the compound, that is, the constituent atoms of the different compounds possess, either individually or collectively, varied affinities for the ammonia group, and for some of the water molecules (water of composition).   This is clearly shown in the following studies, wherein (1) the magnesium atom of $NH_4MgAsO_4.6H_2O$ is substituted by calcium and other metals and (2) the arsenic atom is substituted by phosphorus.

### Ammonium Calcium Arsenate.

The next salt studied was $NH_4CaAsO_4.6H_2O$, which was prepared as follows according to the suggestion of Wach.   Triammonium arsenate (1 part) and ammonium chloride (1 part) were dissolved in a little water and the resulting solution was treated slowly with lime water as long as a precipitate formed.   The precipitate consisted of glistening white crystals; after filtering, washing with alcohol, then with ether, and finally drying on filter paper, they were obtained free from traces of chlorine.   Analysis of the salt gave the following data :

0.3245 grams substance yielded 0.0827 grams CaO = 18.20 per cent. Ca.
0.7757 grams substance yielded 0.0471 grams NH₃ = 5.61 per cent. NH₄.
0.1464 grams substance lost    0.0656 grams at 190°=43.45 per cent. NH₃+H₂O
0.8244 grams substance lost    0.3616 grams at 200°=43.75 per cent. NH₃+H₂O

|  | Theory | Found | Wach[1] | Bloxam[2] |
|---|---|---|---|---|
| AsO$_4$ .......................... | 37.70 | .. .. | 35.83 | 34.92 |
| Ca............................. | 18.36 | 18.20 | 17.52 | 17.29 |
| NH$_4$............................ | 5.90 | 5.61 | 5.37 | 5.28 |
| 6H$_2$O .......................... | 38.04 | .. .. | 41.15 | .. .. |
| NH$_3$ + 6½H$_2$O ............... | 43.93 | 43.75 | .. .. | .. .. |

Evidently the crystals were a purer form of $NH_4CaAsO_4.6H_2O$ than prepared by Wach or by Bloxam. They weathered rapidly; when exposed to air (25°–35°) for four hours they lost 2–20 per cent. in weight.

In the following table the time of decomposition in each case was four hours:

| I Temperature | II Weight salt | III Loss of weight H$_2$O–NH$_3$ | IV NH$_3$ | V H$_2$O | VI Ratio of both | VII Total per cent. H$_2$O+NH$_3$ | VIII NH$_3$ | IX loss of H$_2$O |
|---|---|---|---|---|---|---|---|---|
| 28 | 0.2093 | .0050 | .... | .... | ... | 2.40 | ... | .... |
| 40 | 0.1854 | .0202 | .0006 | .0196 | 32.7 | 10.90 | 0.33 | 10.57 |
| 41 | 0.1482 | .0202 | .0017 | .0185 | 11.0 | 13.63 | 1.12 | 12.51 |
| 44 | 0.1722 | .0396 | .0032 | .0364 | 11.4 | 23.00 | 1.91 | 21.09 |
| 45 | 0.1642 | .0602 | .0055 | .0547 | 10.0 | 36.66 | 3.32 | 33.34 |
| 59 | 0.1920 | .0690 | .0057 | .0633 | 11.1 | 35.94 | 2.97 | 32.97 |
| 59 | 0.1546 | .0562 | .0044 | .0518 | 11.8 | 36.35 | 2.84 | 33.51 |
| 70 | 0.1240 | .0446 | .0035 | .0411 | 11.7 | 35.97 | 2.82 | 33.15 |
| 80 | 0.1798 | .0686 | .0054 | .0652 | 12.1 | 38.15 | 3.00 | 35.15 |
| 90 | 0.1406 | .0564 | .0047 | .0517 | 11.0 | 40.11 | 3.34 | 36.77 |
| 100 | 0.1448 | .0590 | .0051 | .0552 | 10.8 | 40.85 | 3.50 | 37.30 |
| 104 | 0.1310 | .0540 | .0044 | .0496 | 11.3 | 41.22 | 3.37 | 37.85 |
| 110 | 0.1074 | .0440 | .0040 | .0400 | 10.0 | 40.97 | 3.72 | 37.25 |
| 130 | 0.1516 | .0632 | .0059 | .0573 | 9.5 | 41.79 | 3.90 | 37.89 |
| 150 | 0.1448 | .0620 | .0056 | .0564 | 10.0 | 42.82 | 3.86 | 38.96 |
| 170 | 0.1713 | .0740 | .0067 | .0673 | 10.0 | 43.20 | 3.94 | 39.26 |
| 190 | 0.1394 | .0612 | .0060 | .0552 | 8.0 | 43.90 | 4.29 | 39.61 |
| 200 | 0.8244 | .3616 | .... | .... | ... | 43.75 | ... | .... |
| Red heat 0.4172 | .2048 | .... | .... | ... | 49.09 | ... | .... |
| " " 0.3154 | .1536 | .... | .... | ... | 48.70 | ... | .... |

When $NH_4CaAsO_4.6H_2O$ is heated it may sustain any of the following losses or their intermediate per cents.

| Losses of Molecules of | Per cents. of loss |
|---|---|
| NH$_3$............................................. | 5.57 |
| H$_2$O ............................................. | 5.90 |
| 2H$_2$O............................................. | 11.80 |
| 3H$_2$O............................................. | 17.70 |
| 4H$_2$O............................................. | 23.60 |
| 5H$_2$O............................................. | 29.50 |
| 6H$_2$O............................................. | 35.40 |
| 6½H$_2$O............................................. | 38.36 |
| 6½H$_2$O+NH$_3$............................................. | 43.93 |

The above data plotted in the manner of Table I gives the following curves.

[1] Schweigger's J. chim. phys., **59**, 288.
[2] Chem. News, **54**, 168.

PLATE III — DECOMPOSITION OF $NH_4CaAsO_4 \cdot 6H_2O$
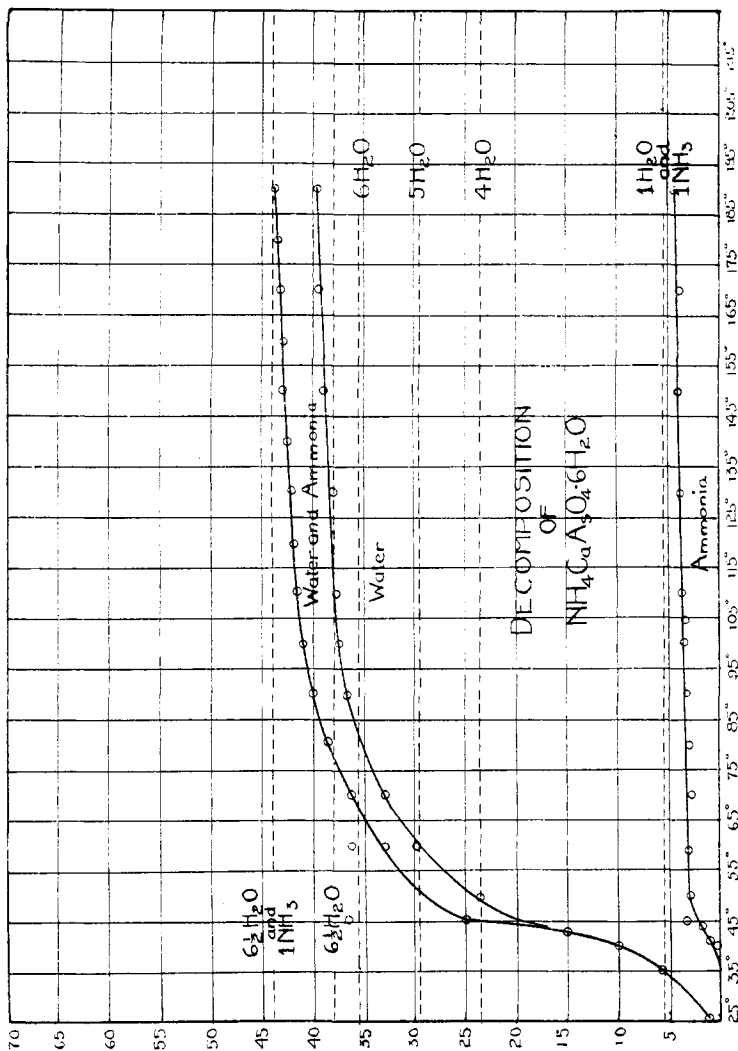
The same misinterpretation of data mentioned in connection with ammonium magnesium arsenate is observed with the calcium salt. Bloxam[1] says on standing 36 days in the air it loses all but one molecule of water; Lefevre[2] says drying at 100° removes all but one-half a molecule of water; Field[3] says it becomes anhydrous at 140°: Kotschubey[4] says it retains one molecule at 125°; and Bloxam[5] assigns formulas $(AsO_4)$-

[1] Chem. News (1886) 54, 168.
[2] Ann. chim. phys. [6] 27, 13.
[3] Jahrsb. 1858, 175.
[4] J. pr. Chem., 49, 188.
[5] Chem. News (1886) 54, 169.

$Ca_3NH_4H_2.3H_2O$ and $(AsO_4)_6Ca_8NH_4H_5.3H_2O$ to the products of drying *in vacuo* over sulphuric acid and drying at 100° respectively.   Failure to recognize the fact that the salt begins to decompose at ordinary temperature, and loses both ammonia and water at higher temperatures accounts for these inconsistencies.
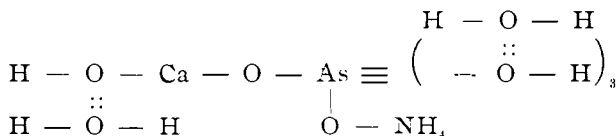
It will be observed that :

1.   Both water and ammonia are given off more easily from the calcium salt than from the corresponding magnesium salt.

2.   The point of greatest decomposition is 40°–50° with the calcium salt instead of 70°–80° as with the magnesium salt.

3.   The temperatures at which all ammonia and water are removed  is 225° with both salts.

4.   The calcium salt like the magnesium salt first liberates one molecule of water then simultaneously three molecules, then one molecule ; then another ; and finally, the one-half molecule derived from the ammonium-oxy group.

Confirmation of the fact that the last two molecules of water differ from the other four, is secured here as with the magnesium salt by studying the alcohol-dehydration products.   The calcium salt was treated twice with alcohol in the same manner as with the magnesium salt ; it then gave the following analytical data :

0.5274 grams substance yielded 0.3600 grams $Mg_2As_2O_7$

0.5279 grams substance yielded 0.3670 grams $Mg_2As_2O_7$

0.3274 grams substance yielded 0.0105 grams $NH_3$

| | Theory | | Found | |
|---|---|---|---|---|
| | $HCaAsO_4.2H_2O$ | $NH_4CaAsO_4.2H_2O$ | I | II |
| As | 34.72 | 32.18 | 33.64 | 33.03 |
| $NH_3$ | 0.00 | 7.32 | 3.20 | |

Evidently the salt lost part of its ammonia and contained just two molecules of water.   All of the evidence, therefore, seems to favor a structural formula that is perfectly analogous to that of $NH_4MgAsO_4.6H_2O$, viz :—

$$H - O - Ca - O - As \equiv \left( \begin{array}{c} H - O - H \\ - \ddot{O} - H \end{array} \right)_3$$

with $H - \ddot{O} - H$ and $O - NH_4$

### Other Alkali Earth Salts.

By treating solutions of triammonium arsenate ( 1 part) and ammonium chloride (1 part) with solutions of strontium hydroxide and barium hydroxide respectively, in exactly the same manner as with calcium hydroxide, it might be expected that the analogous compounds $NH_4SrAsO_4.6H_2O$ and $NH_4BaAsO_4.6H_2O$ would be formed ; the precipitates resulting were found, however, to contain no ammonia and only one

molecule of water. An explanation of this is conceivable when it is recalled that the temperatures of maximum decomposition for the magnesium salt is 70°-80°: for the calcium salt, 40°-50°; and undoubtedly for the strontium and barium salts, below the temperature of formation (room temperature 25°-30°).

The strontium salt prepared in the manner stated was light and fleecy while in suspension and powdery when dry. By dissolving it in hydrochloric acid, adding ammonia to incipient precipitation, filtering and letting stand, the solution yielded beautiful, small, transparent crystals.

I   1.0350 grams powder heated at 350° lost 0.1170 grams

II   0.8820 grams crystals heated at 225° lost 0.0965 grams

| | Theory $HSrAsO_4.H_2O$ | Found I | II |
|---|---|---|---|
| $1\frac{1}{2}$ $H_2O$ | 11.00 | 11.29 | 10.94 |

The barium salt prepared as above yielded small, pearly crystals,

0.6660 grams substance yielded 0.5257 grams $BaSO_4$

0.4365 grams substance heated at 225° lost 0.0375 grams $H_2O$

| | Theory $HBaAsO_4.H_2O$ | Found |
|---|---|---|
| Ba ............................... | 46.44 | 46.41 |
| $1\frac{1}{2}$ $H_2O$ ......................... | 8.59 | 8.60 |

The strontium salt of the above composition had not been prepared hitherto, but undoubtedly its more or less dehydrated form was described by Salkowski[1], Joly[2], Hörman[3], Lefevre[4] and Schiefer[5]. The barium salt is described : Berzelius and Mitscherlich held that it contains one-half molecule of water, the others[6] agree that it contains one molecule of water.

These salts were heated in open crucibles in air baths and yielded the following comparative data :

| Temperature | Hours | $HSrAsO_4.H_2O$ Weight | Loss | Loss per cent. | Per cent. of total $H_2O$ |
|---|---|---|---|---|---|
| 45° | 4 | 0.1152 | .0026 | 2.25 | 20.45 |
| 75° | $1\frac{1}{2}$ | 1.5024 | .0621 | 6.02 | 54.72 |
| 125° | 1 | 1.4923 | .1085 | 7.27 | 66.10 |
| 150° | 1 | 1.5335 | .1151 | 7.56 | 68.72 |
| 210° | $1\frac{1}{2}$ | 0.8612 | .0882 | 10.24 | 95.09 |
| 225° | 1 | 0.8496 | .0938 | 11.04 | 100.40 |
| 350° Red | 1 | 1.0350 | .1170 | 11.29 | 109.63 |
| Heat | $\frac{1}{15}$ | 1.0350 | .1470 | 14.28 | 129.82 |

[1] J. pr. Chem., 1868, 148.

[2] Compt. rend., 104, 905.

[3] Inaug. Diss., 1879.

[4] Ann. chim. phys., (6) 27, 20.

[5] Zeitschrift für die gesammten Naturwissenschaften 23, 564.

[6] J. pr. Chem., 49, 189; Ibid., 104, 159; Ibid., 40, 247, Compt. rend., 58, 253; Lehrbuch der Chemie von Berzelius ; Lehrbuch der Chemie von Mitscherlich.

| Per cent. of total $H_2O$ | Loss per cent. | $HBaAsO_4.H_2O$ Loss | Weight | Hours | Temperature |
|---|---|---|---|---|---|
| 0.85 | 0.07 | .0008 | 1.0914 | 1 | 60° |
| 3.61 | 0.31 | .0050 | 1.6078 | 1 | 115 |
| 29.57 | 2.54 | .0311 | 1.2347 | 1 | 135 |
| 71.59 | 6.15 | .0804 | 1.3067 | 1 | 150 |
| 71.36 | 6.13 | .0986 | 1.6078 | 1 | 190 |
| 95.34 | 8.19 | .0966 | 1.1790 | 1⅓ | 210 |
| 99.88 | 8.58 | .0643 | 0.7496 | 1 | 225 |
| 123.05[1] | 10.57 | .1246 | 1.1790 | ⅕ | Red Heat |

When these salts are heated they suffer the following or intermediate losses:

| | $HSrAsO_4.H_2O$ | $HBaAsO_4.H_2O$ |
|---|---|---|
| $H_2O$ .............................................. | 7.33 | 5.73 |
| $1\frac{1}{2}H_2O$ ........................................... | 11.00 | 8.59 |

and yield the corresponding pyroarsenates. It will be observed in the above table that:

1.  The strontium salt gradually loses its molecule of water below 125°; the barium salt loses its molecule of water below 150°.

2.  Both salts, like the magnesium and calcium salts studied, lose all water at 225°.

The fact that the arsenic atom has no affinity above 225° for the last hydroxyl in these four salts studied shows that there must exist in them the same structure: $As≡O—H$.    Furthermore since these four salts exhibit little difference in the ease of dissociating the last molecule of water, differences that can be attributed to variation of size of salt crystals used, etc., it is tenable that the last molecule of water is held as shown in the structure: $=As—(OH)_3$, consequently the above-mentioned strontium and barium salts must possess the following structural formulas:
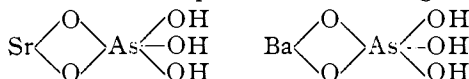
Furthermore it may be gathered from the above experiments that when hydrated ammonium salts, or hydrated salts containing no ammon-

[1] When ammonium calcium arsenate and these two salts are heated in crucibles to temperatures higher than 225°, say by igniting to a red heat, there results to some extent the following reactions: $3M_2As_2O_7 = 2M_3(AsO_4)_2 - As_2O_5$, $As_2O_5 = As_2O_3 + O_2$. Evidences for these reactions are as follows: first, the residue, easily soluble in hydrochloric acid, shows the presence of arsenate, but no arsenite; secondly, a sublimate obtained on heating in tubes, yields tests for both oxides. This loss with the calcium salt was mentioned by Wach[2] and Lefevre[3]; the second reaction is described by Kopp[4]; the stability of $Ca_3(AsO_4)_2$ toward heat is confirmed by Simon[5].

[2] Schwiegger's J. Chem. Physik., 59, 265.

[3] Ann. chim. phys., (6) 27, 56.

[4] Ibid, (3) 48, 106; Jahrsb., 1856, 385.

[5] Ann. Physik. ü Chem., Pogg., 40, 417.

ia begin to decompose, *fractions from each molecule of water (and of the ammonia) are given off at all temperatures lower than the ones at which individually they are completely dissociated;* therefore, for instance in $NH_4MgAsO_4.6H_2O$, from which 1 mol. $NH_3$, 1 mol. $H_2O$, 3 mols. $H_2O$, 1 mol. $H_2O$, and 1 mol. $H_2O$ are separately dissociated, *all of the higher dissociations are taking place fractionally and simultaneously when any of the lower dissociations are taking place partially or completely*, hence within the range of temperatures of dissociation, *no definite formula can be assigned to the residues.*

### Salts of Phosphoric Acid.

It was shown above that substitution of alkali earths elements in $NH_4MgAsO_4.6H_2O$ produced complexes more easily decomposed than the magnesium salt; it now remains to show the effect of substitution of phosphorus for arsenic in $NH_4MgAsO_4.6H_2O$. It was found as a matter of fact that this salt, though more stable than the arsenic salts, decomposes in the same manner and consequently must possess a similar struc-

$$ \begin{array}{c} H \cdot O - H \\ \\ \text{tural formula:} \quad H - O - Mg - P \cdot (-O - H)_4. \\ \\ H - O - H \quad O - NH_4 \end{array} $$

The samples of $NH_4MgPO_4.6H_2O$ used were found by ignition to be absolutely pure; and in the following experiments were heated for four hours, except fractions indicated by temperatures 148-205°, which were heated for 7 hours each (table IV).

When heated, $NH_4MgPO_4.6H_2O$ may sustain any of the following molecular loses or their intermediate per cents:

| Loss of Molecules of | Per cent. of loss |
|---|---|
| $NH_3$ | 6.93 |
| $H_2O$ | 7.34 |
| $2H_2O$ | 14.70 |
| $3H_2O$ | 22.04 |
| $4H_2O$ | 29.39 |
| $5H_2O$ | 36.74 |
| $6H_2O$ | 44.08 |
| $6\frac{1}{2}H_2O$ | 47.34 |
| $6\frac{1}{2}H_2O - NH_3$ | 54.70 |

It is seen on comparing Plates II and IV that:

1. Both ammonium magnesium arsenate and ammonium magnesium phosphate sustain maximum decompositions between 70° and 80°.

2. The former begins to decompose below 40°; the latter at 45°.

3. The former is completely decomposed at 225°; the latter is not completely decomposed at 360°.

4. Half of the ammonia of the former is liberated below 80°; half of the ammonia of the latter is liberated below 155°.

TABLE IV

| I Temperature | II Weight of Salt | III Loss of H₂O+NH₃ | IV weight of NH₃ | V weight of H₂O | VI Ratio of Both | VII Total per cent. H₂O+NH₃ | VIII Total per cent. NH₃ | IX Total per cent. loss of H₂O |
|---|---|---|---|---|---|---|---|---|
| 40 | .5810 | .0000 | .0000 | .0000 | 0.0 | 0.00 | 0.00 | 0.00 |
| 45 | .9808 | .0060 | .0005 | .0055 | 11.0 | 0.61 | 0.05 | 0.56 |
| 50 | .4926 | .0120 | .0009 | .0111 | 12.3 | 2.44 | 0.18 | 2.26 |
| 55 | .3129 | .0108 | .0006 | .0102 | 17.0 | 3.26 | 0.19 | 3.07 |
| 60 | .5400 | .0193 | .0016 | .0177 | 11.1 | 3.57 | 0.30 | 3.27 |
| 65 | .4921 | .0247 | .0020 | .0227 | 11.3 | 5.02 | 0.41 | 4.61 |
| 70 | .7473 | .0423 | .0042 | .0381 | 9.1 | 5.66 | 0.56 | 5.10 |
| 76 | .5140 | .1763 | .0030 | .1463 | 48.8 | 34.30 | 0.59 | 33.71 |
| 80 | .6504 | .2341 | .0040 | .2301 | 57.5 | 36.00 | 0.61 | 35.39 |
| 95 | .2254 | .0822 | .0016 | .0806 | 50.4 | 36.47 | 0.71 | 35.76 |
| 110 | .4260 | .1557 | .0032 | .1525 | 47.9 | 36.55 | 0.75 | 35.80 |
| 127 | .1674 | .0624 | .0013 | .0611 | 47.0 | 37.28 | 0.77 | 36.51 |
| 135 | .1249 | .0487 | .0010 | .0477 | 47.7 | 39.06 | 0.80 | 38.26 |
| 148 | .1620 | .0664 | .0021 | .0643 | 30.5 | 40.98 | 1.30 | 40.68 |
| 155 | .1126 | .0514 | .0040 | .0474 | 11.8 | 45.65 | 3.55 | 42.10 |
| 165 | .0926 | .0436 | .0041 | .0395 | 9.6 | 47.08 | 4.42 | 42.66 |
| 175 | .0900 | .0436 | .0043 | .0393 | 9.1 | 48.45 | 4.77 | 43.68 |
| 186 | .0680 | .0336 | .0033 | .0303 | 9.2 | 49.41 | 4.85 | 44.56 |
| 195 | .0526 | .0260 | .0026 | .0234 | 9.0 | 49.50 | 4.94 | 44.56 |
| 200 | .1251 | .0624 | .0065 | .0559 | 8.6 | 49.88 | 5.19 | 44.69 |
| 205 | .1387 | .0702 | .0073 | .0629 | 8.6 | 50.61 | 5.26 | 45.35 |
| 225 | .4734 | .2342 | .... | .... | .. | 50.53 | .... | .... |
| 230 | .9374 | .4726 | .... | .... | .. | 50.52 | .... | .... |
| 240 | .9374 | .4818 | .... | .... | .. | 51.39 | .... | .... |
| 295 | .9374 | .4950 | .... | .... | .. | 52.50 | .... | .... |
| 310 | .6631 | .3494 | .... | .... | .. | 52.70 | .... | .... |
| 340 | .6631 | .3514 | .... | .... | .. | 53.00 | .... | .... |
| 360 | .3194 | .1704 | .... | .... | .. | 53.33 | .... | .... |
| Red heat. | 8724 | .4767 | .... | .... | .. | 54.63 | .... | .... |

5. With both salts, first one molecule of water is liberated : then simultaneously, three molecules ; then one molecule; again one molecule; and finally the last one-half molecule[1].

When $NH_4MgPO_4.6H_2O$ was heated with alcohol in the manner that the corresponding arsenic salt was, similar dehydration and removal of ammonia were incurred. After a sample was heated for three hours, it gave the following analytical data :

0.4522 grams lost by ignition 0.1460 grams = 32.29 per cent.
0.4057 grams lost by ignition 0.1230 grams = 32.04 per cent.
Average = 32.16 per cent.
0.1651 grams yielded 0.0026 gram $NH_3$ = 1.59 per cent.
Therefore $H_2O$ = 32.16 − 1.59 = 30.57 per cent.

[1] Here as with the corresponding arsenic salt, *five* molecules of water are apparently given off simultaneously ; the explanation here is the same as there.—The curve here shows a liberation of *one* molecule of water below 67°. This harmonizes with the above formula wherein the molecule of water attached to H—O—Mg—O— differs from the other three molecules of "water of crystallization."

PLATE IV.

DECOMPOSITION OF $NH_4MgPO_4.6H_2O$
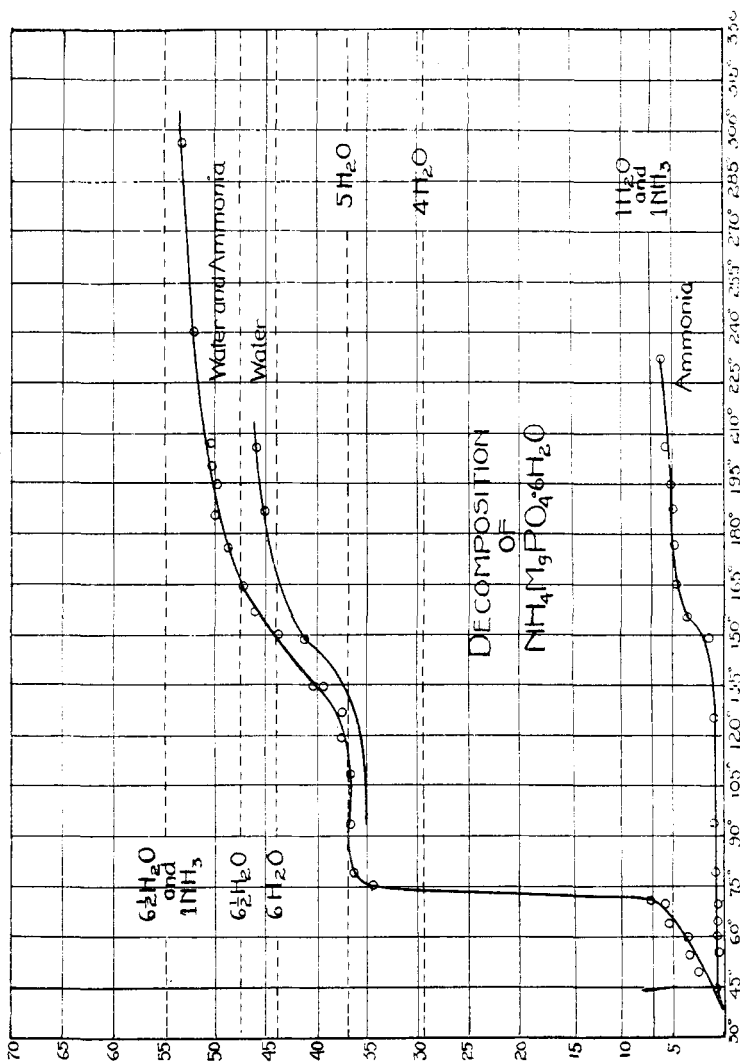
Another sample was heated for two hours with alcohol and the treatment with alcohol was repeated: the salt then gave the following analytical data:

0.4539 grams lost by ignition 0.3189 grams = 29.74 per cent.
0.4002 grams lost by ignition 0.2811 grams = 29.79 per cent.
Average = 29.76 per cent.
0.0676 grams yielded 0.0006 grams $NH_3$ = 0.89 per cent.
0.1201 grams yielded 0.0011 grams $NH_3$ = 0.95 per cent.
Average = 0.92 per cent.
Therefore $H_2O$ 29.76 — 0.92 = 28.84 per cent.
Theory of $H_2O$ in $HMgPO_4.2H_2O$ = 28.84 per cent.

Therefore, upon heating ammonium magnesium phosphate with alcohol the following reaction takes place :

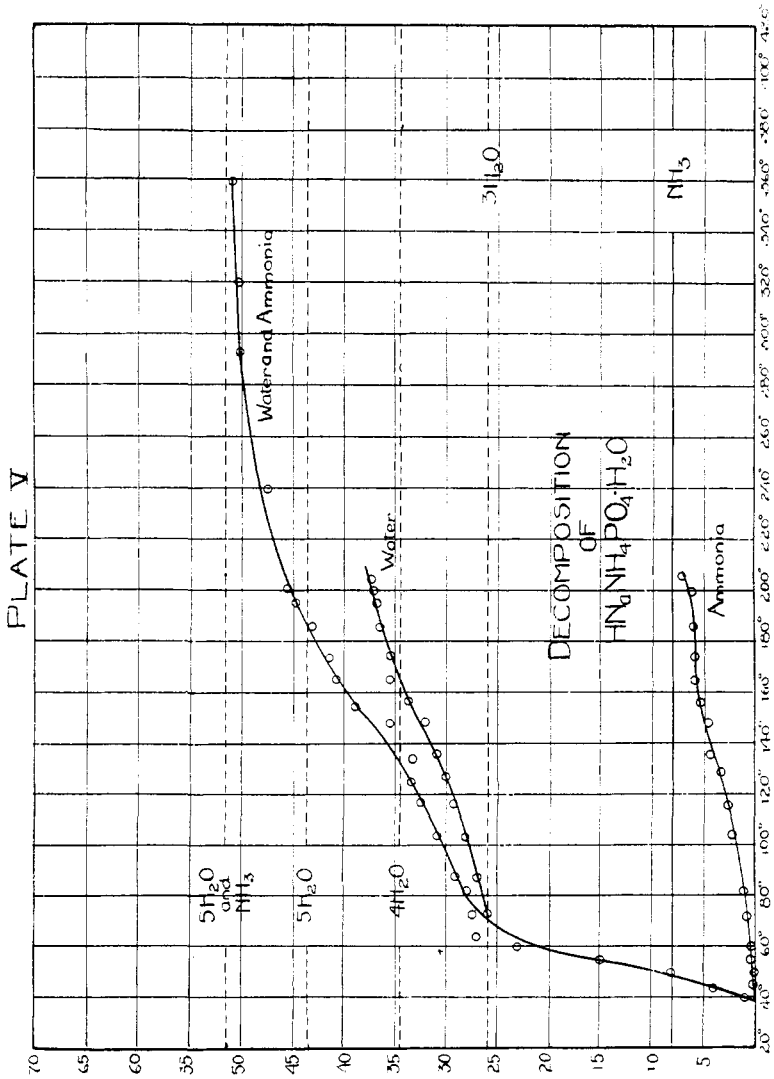$$NH_4MgPO_4.6H_2O = HMgPO_4.2H_2O + 4H_2O + NH_3$$
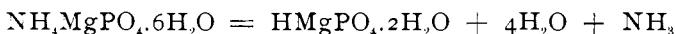
### Microcosmic Salt.

This salt yielded comparative data with greater difficulty than any other salt studied. The cause of this was ultimately found to be owing to variations in size of crystals used. After pulverizing and passing them through the sieve, little difficulty was encountered.

| I Temper- ature | II Time | III Weight of Salt | IV Loss of weight of $H_2O-NH_3$ | V $NH_3$ | VI $H_2O$ | VII Ratio of Both | VIII Total per cent. $H_2O+NH_3$ | IX $NH_3$ | X loss of $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 4 | 2.1818 | .0254 | .0008 | .0246 | 30.7 | 1.16 | 0.04 | 1.12 |
| 45 | 4 | 1.3590 | .0498 | .0009 | .0489 | 54.4 | 3.66 | 0.07 | 3.59 |
| 50 | 4 | 0.9220 | .0788 | .0009 | .0779 | 86.5 | 8.55 | 0.10 | 8.45 |
| 55 | 4 | 0.3876 | .0683 | .0013 | .0670 | 51.5 | 17.62 | 0.36 | 17.26 |
| 60 | 4 | 0.4848 | .1138 | .0020 | .1118 | 55.9 | 23.26 | 0.43 | 22.93 |
| 64 | 3 | 0.4520 | .1226 | .0032 | .1194 | 37.3 | 27.13 | 0.71 | 26.42 |
| 72 | 4 | 0.1205 | .0332 | .0011 | .0321 | 29.2 | 27.61 | 0.89 | 26.72 |
| 83 | 3 | 0.4439 | .1262 | .0054 | .1208 | 22.3 | 28.44 | 1.23 | 27.21 |
| 88 | 4 | 0.8261 | .2404 | .0124 | .2280 | 18.4 | 29.10 | 1.50 | 27.60 |
| 104 | 4 | 0.4764 | .1477 | .0105 | .1372 | 13.0 | 31.00 | 2.20 | 28.80 |
| 116 | 4 | 0.2786 | .0801 | .0078 | .0723 | 9.3 | 32.75 | 2.80 | 29.45 |
| 127 | 4 | 0.1898 | .0630 | .0063 | .0567 | 9.0 | 33.29 | 3.32 | 29.97 |
| 135 | 4 | 0.1656 | .0586 | .0071 | .0515 | 7.2 | 35.39 | 4.29 | 31.10 |
| 148 | 4 | 0.2310 | .0840 | .0105 | .0735 | 7.0 | 36.46 | 4.54 | 31.92 |
| 155 | 4 | 0.1219 | .0477 | .0064 | .0413 | 6.4 | 39.13 | 5.49 | 33.64 |
| 165 | 4 | 0.1664 | .0680 | .0095 | .0585 | 6.1 | 40.86 | 5.70 | 35.16 |
| 175 | 4 | 0.1026 | .0422 | .0058 | .0364 | 6.3 | 41.13 | 5.65 | 35.48 |
| 186 | 4 | 0.0680 | .0289 | .0039 | .0250 | 6.4 | 42.50 | 5.74 | 36.76 |
| 195 | 4 | 0.0818 | .0364 | .0050 | .0314 | 6.3 | 44.50 | 6.11 | 38.39 |
| 200 | 4 | 0.1016 | .0459 | .0063 | .0396 | 6.3 | 45.18 | 6.20 | 38.98 |
| 205 | 4 | 0.1648 | .0758 | .0122 | .0636 | 5.2 | 46.00 | 7.40 | 38.60 |
| 240 | 2 | 0.6130 | .2235 | .... | .... | .. | 46.95 | | |
| 295 | 2 | 1.2261 | .6154 | .... | .... | .. | 50.19 | | |
| 310 | 4 | 1.0204 | .5152 | .... | .... | .. | 50.49 | | |
| 360 | 3 | 0.5070 | .2558 | .... | .... | .. | 50.40 | | |
| Red heat | 1/5 | 0.9328 | .4760 | .... | .... | .. | 51.02 | | |

When microcosmic salt decomposes it may sustain any of the following or intermediate losses :

$NH_3$................................................................. 8.13
$H_2O$. ...... ....................................................... 8.61
$2H_2O$ .............................................................. 17.22
$3H_2O$ ..... ....................................................... 25.83
$4H_2O$ ............................................................. 34.45
$5H_2O$ ............................................................. 43.05
$4H_2O-NH_3$ ....................................................... 42.58
$5H_2O+NH_3$ ...................................................... 51.20

PLATE V

DECOMPOSITION OF $HNaNH_4PO_4 \cdot H_2O$

It is observed that :

1. Three molecules of water are expelled simultaneously below 62°.

2. The fourth molecule of water is expelled below 160°.

3. The last molecule of water here as with ammonium magnesium phosphate is not completely removed at 360°.

4. The ammonium molecule is expelled in nearly the same manner as with ammonium magnesium phosphate.

All of the facts seem to support the following structural formula for microcosmic salt :

$$\begin{matrix} & & \text{HOH} \\ \text{Na—O} & & :: \\ & \!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\! \diagdown\!\!\diagup\ \text{P}\!\equiv\!(\text{OH})_3 \\ \text{NH}_4\text{—O} & & \end{matrix}$$
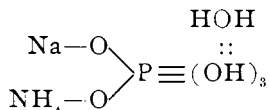
which upon being heated liberates first the three molecules of water held
by tetravalent oxygen ; then the molecule derived from two hydroxy
groups ; and finally the molecule of water derived from the ammonium-
oxy and the remaining hydroxyl group.

Further evidence that microcosmic salt contains three molecules of
water that are similar in the ease of dissociating, and consequently that
they possess similar structural attachments, is derived by the alcohol-dehy-
dration method.    After heating twice with alcohol for one hour, the
residue contained 9.60 per cent. ammonia and yielded, by ignition, a
loss of 45.70 per cent., or a loss of only a fraction of one molecule of
water had been sustained.

### Vapor Pressure Determinations.

When the vapor pressures of ammonium magnesium arsenate are care-
fully determined a distinct break in its curve (vide Plate VI) is notice-
able below 35°, indicating the liberation of one molecule of water at this
temperature.    The following data represent two different determinations:

SERIES I

| Temperature | Pressure | Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|---|---|
| 27 | 0.61 | 37 | 6.96 | 45 | 11.70 |
| 28 | 0.92 | 38 | 7.62 | 46 | 13.08 |
| 29 | 1.23 | 39 | 7.65 | 47 | 13.80 |
| 32 | 2.48 | 40 | 7.67 | 48 | 14.50 |
| 34 | 4.36 | 41 | 9.01 | 49 | 15.90 |
| 35 | 5.65 | 43 | 9.70 | 50 | 17.30 |
| 36 | 6.30 | 44 | 10.40 | 51 | 19.40 |

SERIES II

| Temperature | Pressure | Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|---|---|
| 31.5 | 3.00 | 35.5 | 7.50 | 44 | 10.6 |
| 32.0 | 4.25 | 40.5 | 8.00 | 49 | 14.5 |
| 33.0 | 5.50 | 42.0 | 9.30 | 54 | 18.0 |

When this salt is heated at once to temperatures of 70°–98°, other con-
ditions remaining the same, the phenomenon of "suspended transform-
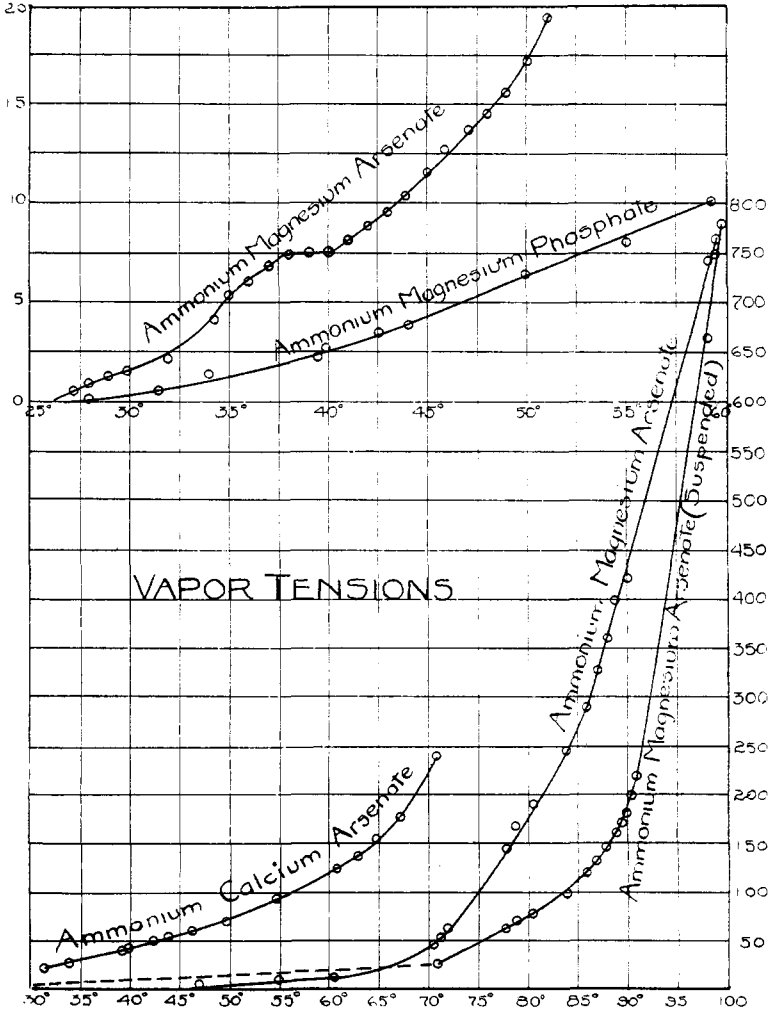ation" becomes manifest, as is shown in Plate VI and the following
data :

SUSPENDED TRANSFORMATION

| Temperature | Pressure | Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|---|---|
| 30.0 | 10.70 | 86. | 120.5 | 90. | 186 |
| 71.2 | 29.02 | 86.9 | 136.8 | 90.5 | 204 |
| 78.0 | 65.26 | 88. | 150. | 91. | 225 |
| 79.0 | 73.92 | 89. | 167. | 98. | 670 |
| 80.3 | 81.88 | 89.4 | 177. | 98.7 | 776 |
| 83.8 | 101.75 | | | | |

NON-SUSPENDED TRANSFORMATION

| Temperature | Pressure | Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|---|---|
| 45.5 | 1.39 | 72 | 65.5 | 88. | 364.5 |
| 47.0 | 6.54 | 78 | 148.7 | 89 | 404.8 |
| 50.2 | 7.11 | 79 | 169.0 | 89.4 | 417.0 |
| 55.2 | 9.38 | 80.3 | 194.0 | 90 | 424.0 |
| 60.6 | 14.79 | 81.4 | 219.8 | 91 | 482.0 |
| 64.0 | 21.78 | 83.8 | 247.3 | 92 | 559.0 |
| 70.5 | 45.27 | 86 | 291.0 | 98 | 745.1 |
| 71.2 | 53.54 | 87 | 331.5 | | |



PLATE VI

VAPOR TENSIONS

Though the general forms of these two curves are similar. it is observed
(1) that the normal pressures are not exerted when the salt is heated *at*

*once to 70°* and (2) that this condition of suspended transformation is lost at 99°. Evidently the cause of this condition is the formation of a superficial impervious layer of dehydrated substance that protects the inner portions from immediate decomposition.

The vapor pressures of the other curves are given in the following tables :

### AMMONIUM CALCIUM ARSENATE[1].

| Temperature | Pressure | Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|---|---|
| 31.5 | 25.6 | 44.0 | 55.2 | 62.7 | 136.9 |
| 34.0 | 29.5 | 46.5 | 61.2 | 65.1 | 161.6 |
| 39.4 | 40.8 | 50.0 | 73.6 | 67.4 | 188.3 |
| 40.0 | 45.3 | 55.0 | 93.6 | 70.2 | 222.7 |
| 42.5 | 50.5 | 60.8 | 124.5 | 70.8 | 246.3 |

### AMMONIUM MAGNESIUM PHOSPHATE[1].

| Temperature | Pressure | Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|---|---|
| 28.0 | 10.36 | 40.0 | 12.82 | 50.0 | 16.54 |
| 31.5 | 10.79 | 42.5 | 13.26 | 55.0 | 17.92 |
| 34.0 | 11.57 | 44.0 | 14.06 | 58.5 | 20.02 |
| 39.4 | 12.43 | 46.5 | 15.27 | | |

### VAPOR PRESSURES[2]

| Temperature | $HNaNH_4PO_4.4H_2O$ | $NH_4MgAsO_4.6H_2O$ | $NH_4MgPO_4.6H_2O$ | $NH_4CaAsO_4.6H_2O$ |
|---|---|---|---|---|
| 30.6 | ... | ... | 30.0 | ... |
| 32.8 | ... | ... | 32.0 | 19.5 |
| 35.0 | ... | 14.5 | 37.0 | 25.3 |
| 39.0 | 12.0 | 23.0 | 47.0 | 34.0 |
| 42.2 | 17.0 | ... | 54.3 | 45.0 |
| 45.0 | 30.0 | ... | 61.5 | ... |
| 47.8 | ... | 30.3 | 75.0 | 65.6 |
| 48.0 | ... | 33.0 | 77.0 | 69.0 |
| 52.5 | 44.0 | 58.0 | ... | ... |
| 55.0 | 45.5 | ... | 89.0 | 106.0 |
| 55.3 | ... | ... | 95.5 | 117.0 |
| 56.8 | ... | ... | 120.0 | 141.0 |
| 59.0 | 65.0 | 70.0 | 132.5 | 217.0 |
| 61.0 | 73.0 | 84.0 | 151.0 | 246.5 |
| 64.5 | 85.0 | 85.0 | 176.5 | 390.0 |
| 68.7 | 113.0 | 125.0 | 215.0 | 407.0 |
| 70.8 | 134.0 | 137.5 | 239.0 | ... |
| 71.2 | 148.3 | 154.0 | 240.6 | ... |
| 75.0 | 170.0 | 212.0 | 273.0 | ... |
| 78.0 | 201.0 | 267.0 | 330.2 | ... |
| 82.5 | 252.5 | 405.0 | 418.0 | ... |

[1] All vapor pressures mentioned thus far were determined in Dehn's tensimeter. (This Journal, 29, 1052.) The break in the curve represented by the expulsion one of molecule of water from ammonium magnesium phosphate is not plainly marked ; however the vapor pressures here were not determined with the greatest of care.

[2] These vapor pressures were determined in the Bremer-Frowein form of tensimeter (Phys. Chem., 1, 5; 17, 52), and, being only approximately correct, are useful here only in showing relative pressures at higher temperatures.

## PLATE VII
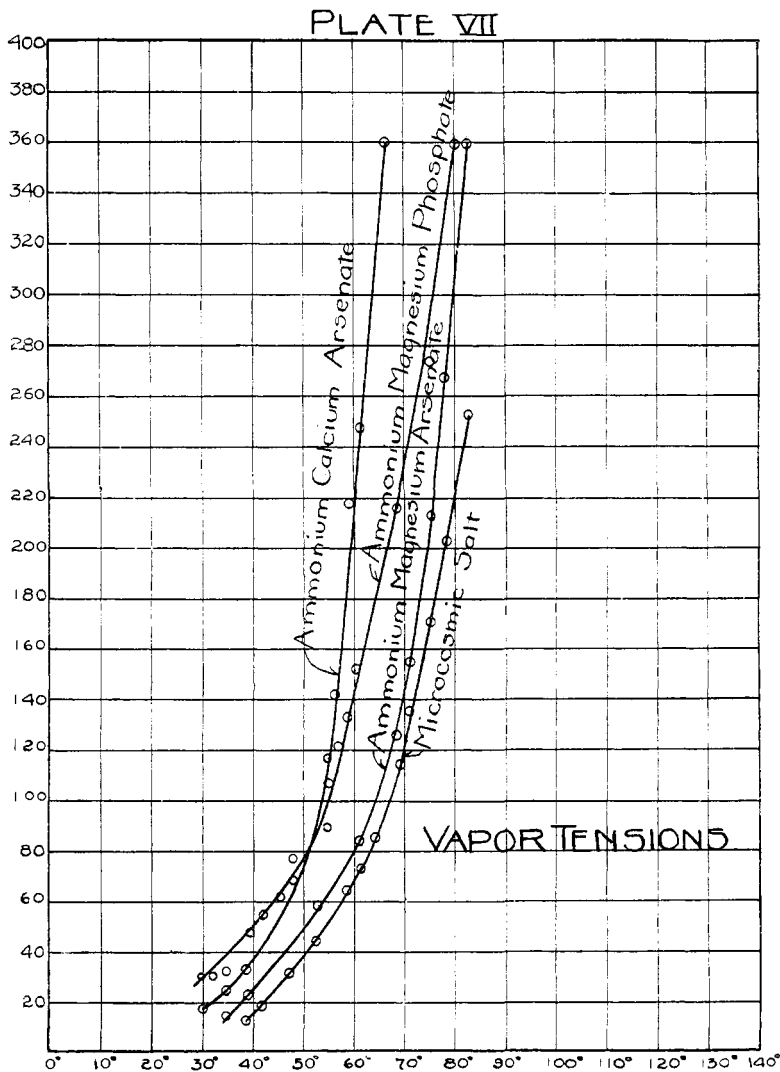


Further studies by the methods herein expressed are being made; at present one may safely draw the following:

### Conclusions.

1.    Hydrated ammonium salts upon being partially or largely dehydrated yield products of indefinite composition, for the reason that

2.    These salts at elevated temperatures undergo primary or secondary decompositions of all of the different dissociating molecules of water and ammonia, consequently

3.   Drying on the water-bath or "drying to constant weight" cannot yield homogeneous products, and therefore,

4.   Many of the empirical formulas of such compounds given in the literature are necessarily incorrect.

5.   The affinity and manner of union of water of composition do not differ largely from the affinity and manner of union of ammonia.

6.   Water of crystallization, conforming to the law of definite proportions, must be held in definite molecular structures, through the agency of valency, as in other compounds.

7.   Tetravalent oxygen, necessary to express these structures, is loosened at temperatures above 100°, therefore salts usually expell water of crystallization below this temperature and water of composition above this temperature.

8.   Finding dissimilar molecules of water in hydrated salts, leads to a conception of their structure.

URBANA, ILLINOIS.
May 29, 1907.

---

## THE SPECIFIC HEAT OF SOLIDS AT CONSTANT VOLUME, AND THE LAW OF DULONG AND PETIT.

BY GILBERT NEWTON LEWIS.

The study of the relation between the specific heat of gases at constant volume and at constant pressure has led to a number of important theoretical conclusions, but in the case of solids and liquids we have been familiar hitherto only with the specific heat at constant pressure.   To determine experimentally the specific heat at constant volume of a liquid or solid would be a difficult undertaking.   Fortunately it is possible, assuming nothing more than the validity of the two laws of thermodynamics, to calculate this important quantity from existing data.

The internal energy at constant temperature is nearly independent of the volume, in the case of a gas, but may vary considerably with the volume in the case of a liquid or solid.   Except in rare cases it increases with increasing volume.   The difference between the specific heats at constant pressure and constant volume is chiefly due to this change of internal energy with the volume, as I have shown in a previous paper[1] where the following purely thermodynamic equation was obtained.

$$c_p - c_v = \left(\frac{\partial v}{\partial T}\right)_P \left[ P + \left(\frac{\partial E}{\partial v}\right)_T \right] \qquad (1)$$

$c_p$ and $c_v$ are the two specific heats.   E and $v$ are respectively the in-

[1] Lewis.   The Development and Application of a General Equation for Free Energy and Physico-Chemical Equilibrium Equation 38.   Pr. Am. Acad., **35**, 1 (1899) ; J. physic. Chem., **32**, 364 (1900).