CLXX.—*The Vapour Density of Ammonium Nitrate, Benzoate, and Acetate.*

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In continuation of the work on the vapour density of ammonium nitrite (T., 1912, **101**, 1185), that of ammonium nitrate has been investigated. Preliminary trials showed that ammonium nitrate begins to sublime very slowly in a vacuum at about 180°, and as complete vaporisation of the substance requires a much higher temperature, Hofmann's method was found to be impracticable, for at a temperature much higher than 200° mercury has an appreciable vapour tension. In these circumstances, the apparatus adopted was that described by Bleier and Kohn (*Monatsh.*, 1899, **20**, 505), with the difference that the outer jacket used was of iron.

Ammonium Nitrate.

The sublimation of ammonium nitrate takes place in the vacuum of the Sprengel pump at a temperature of about 180°. Since at the boiling point of nitrobenzene (208°) no appreciable vaporisation was obtained, bromobenzene (b. p. 280°) was employed in the outer jacket, the upper part of which was wrapped with cotton wool and asbestos, to diminish loss of heat by radiation.

In order to determine the constant of the apparatus—that is, the increase of pressure caused by the vaporisation of a millimolecule of substance at the temperature of the experiment—nitrobenzene (b. p. 208°), benzyl alcohol (b. p. 206°), and methyl salicylate (b. p. 224°) were chosen as standard substances. The first substance gave somewhat anomalous results, due probably to a slight charring of the substance, which could be observed when the tube was taken out after the experiment was finished. The second and the third substances, however, gave satisfactory results. As a mean of several experiments, the constant obtained was 196·7.

	Wt. in milligrams.	*P.* in mm.	*C.*
Methyl salicylate	83·4	108·5	197·7
	101·4	130·5	195·5
	96·2	121·5	192·0
Benzyl alcohol	61·6	114·0	201·0
	64·2	117·5	197·7
		Mean.....	196·7

A small tube, containing a weighed quantity of ammonium nitrate, was introduced into the apparatus, and allowed to remain at the "catch." The apparatus was then exhausted, and the

mercury in the manometer was allowed to rise to the mark. The pressure in the apparatus was nearly 80 mm. The connexion with the pump was then cut off, and the whole allowed to remain for two to three minutes to ascertain whether the mercury remained stationary at the mark. If this was so, the weighed tube was allowed to drop in by a gentle pull at the "catch." The vaporisation began in a minute, and was completed in about eight to ten minutes. The mercury level was adjusted, and it was found that in about ten to twelve minutes the thread began to rise, indicating that condensation of the products had set in. The maximum reading was therefore taken. The apparatus was then allowed to cool for some time until the temperature fell to about 90°. The products were then drawn off by the Sprengel pump and collected in a graduated tube over mercury. This gas, on analysis, was found to contain air and nitrous oxide only. Not a trace of ammonia or nitric oxide could be detected in it.

The apparatus was now disconnected. Small crystals of ammonium nitrate could be seen deposited in the cooler parts of the neck. The vaporising globe and the stem were washed with as small a quantity of water as possible. The wash-water was treated in a Crum-Frankland nitrometer. The gas produced was found to be nitric oxide. In one experiment the quantity of ammonium nitrate, corresponding with the amount of nitric oxide and nitrous oxide, was found to be 0·0185 gram, whilst the quantity actually taken was 0·0192 gram.

Calculation of the Vapour Density.—The density of the mixed gases, consisting of nitrous oxide, water vapour, and ammonium nitrate vapour, was calculated by means of the formula $d = cw/2p$. 41·4 Milligrams of ammonium nitrate produced a difference of pressure of 224 mm. The value of C was known to be 196·7, and from this the density was found to be 18·10. Now, the volume of nitrous oxide determined in the residual air from the vaporising globe was 3·05 c.c. at N.T.P.* The amount of ammonium nitrate corresponding with this volume of nitrous oxide was 10·86 milligrams from the equation: $NH_4NO_3 = 2H_2O + N_2O$.

Now, the volume of the mixed gases was found from the weight of the substance originally taken, and the density by means of the formula $w = v \times d \times 0{\cdot}000089$ g. This volume was 25·69 c.c. From this, the volume of N_2O and $2H_2O$ was deducted, and the value was 16·54 c.c. From the weight of the undecomposed ammonium nitrate, which is (41·4 − 10·86) 30·54 milligrams, and the volume

* The nitrous oxide was removed by repeatedly shaking it with tap-water and changing the solvent four or five times until no more diminution in volume was noticed. Blank experiments in which mixtures of air and nitrous oxide in varying proportions were similarly treated proved the trustworthiness of this method.

occupied by it in the gaseous state, which is 16·54 c.c., we find the density to be 20·70.

The following results are calculated in a similar way from other experiments:

	Weight in milligrams.	*P.* in mm.	Vol. of N_2O at N.T.P.	Weight of NH_4NO_3 corresponding with N_2O.	Calculated density.
II.	17·4	103·5	2 321	8·26	21·08
III.	38·3	233·0	5·034	17·92	19·89
IV.	22·1	134·5	3·221	11·47	20·90
V.	95·5	537·0	9·616	33·99	21·47
VI.	37·4	206·2	2·159	7·686	19·51
VII.	39 5	200·0	1·623	5·776	21·07

As a mean of these experiments, the vapour density is found to be 20·66. It is evident, then, that at a temperature of 280° and under a pressure of 80 mm., the dissociation of ammonium nitrate is complete; a part of the salt at the same time decomposes into nitrous oxide and water.

Veley has shown that molten ammonium nitrate shows an acid reaction due to the presence of nitric acid (T., 1883, **43**, 370). This is explained by the fact that the substance decomposes into ammonia and nitric acid, but as the former diffuses off more rapidly than the latter, the molten mass acquires an acid reaction.

In order to settle this point more satisfactorily, a quantity of ammonium nitrate was placed in a glass tube, sealed at one end, in which a porous diaphragm was interposed. A strip of red litmus paper was then introduced into the drawn-out portion. This end was then connected with the Sprengel pump, and when the requisite vacuum was attained the tube was immersed in a bath of paraffin heated at about 260°, and the pump allowed to work. After a few minutes the strip became blue, and subsequently red again, showing that dissociation takes place, the ammonia diffusing more rapidly than the nitric acid.

A few experiments were conducted in which the vapour density apparatus was previously partly filled with ammonia. It was noticed that the amount of ammonium nitrate which decomposed under this condition was appreciably less. Thus, in one experiment, using 0·065 gram of the salt, we obtained only 1·8 c.c. of nitrous oxide. This is quite in agreement with the results of Veley, who found that on passing ammonia into molten ammonium nitrate, the decomposition of the substance was completely arrested (*loc. cit.*).

Ammonium Benzoate and Acetate.

Preliminary experiments showed that ammonium acetate melts at about 85° in a vacuum. It rapidly loses ammonia, which can be

collected at the end of the Sprengel pump. It can be sublimed very slowly; the greater part of it, however, undergoes dissociation, and much free acetic acid is left behind. Ammonium benzoate can be sublimed at 160° without melting. There is rapid evolution of ammonia, and a mixture of ammonium benzoate and benzoic acid is deposited. The lower part of the tube contains, however, almost pure ammonium benzoate.

For the determination of the vapour density of these substances a bath of nitrobenzene (b. p. 208°) was used. The constant of the apparatus was determined by means of benzene. The following results were obtained with ammonium benzoate:

Weight in milligrams.	*P* in millimetres.	*d*.
15·5	25	40·4
18·8	29	42·3
19·2	29	43·2
25·6	38	44·0

The theoretical value of the density for complete dissociation is 34·75. The high values obtained in the experiment are due to the fact that in each case small, feathery crystals of benzoic acid were found deposited at the neck of the tube. In order to avoid this, very small quantities of the salt were taken, but in this case the experimental errors vitiated the results, and the time required for complete vaporisation was even here long enough to allow of the deposit of some benzoic acid crystals at the neck through diffusion. The easy condensability of benzoic acid made it extremely difficult to determine the vapour density with accuracy. The above table shows that with increased quantities of the salt the value of the density increases. This is because the time required for complete vaporisation increases, and so the diffusion is greater and larger quantities of the acid are condensed at the neck.

In the case of ammonium acetate this difficulty is overcome, as the acetic acid vapour is not so easily condensable. The following table gives the result in this case:

Weight in milligrams.	*P*. in mm.	*d*.
65·0	208	20·4
65·8	218	19·7
89·0	289	20·1

The calculated value of the density for complete dissociation is 19·3. It is proved, therefore, that in this case also complete dissociation of the substance takes place.

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