91. *The Decomposition of Ammonium Nitrate.*

By MADHAVLAL SUKHLAL SHAH and TRAMBAKLAL MOHANLAL OZA.

THE decomposition of ammonium nitrate has been studied by various investigators. Emmet (*Amer. J. Sci.*, 1830, **18**, 255) showed that, like other ammonium salts, when exposed to the air or when heated it lost ammonia, becoming acid :

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 - 41{\cdot}30 \text{ Cals.} \quad . \quad (1)$$

The decomposition into nitrous oxide and water, which has been long known, was studied by Berthelot (*Compt. rend.*, 1876, **82**, 932), Thomsen (*Ber.*, 1879, **12**, 2062), and Veley (J., 1883, **43**, 370). The first two found that the reaction is exothermic :

$$\begin{aligned} NH_4NO_3 \longrightarrow N_2O + 2H_2O &+ 29{\cdot}5 \text{ Cals. (B.)} \\ &+ 30{\cdot}34 \text{ Cals. (T.)} \quad . \quad . \quad (2) \end{aligned}$$

The last studied the rate of decomposition by measuring the gas evolved and the free acid formed, and concluded that it "is dependent, not only on the mass of ammonium nitrate undergoing decomposition, but also upon the proportion of free acid present," and that it is completely arrested even at temperatures 50—60° above the normal decomposition temperature by an excess of ammonia obtained either by passing in the gas or by the addition of a basic oxide.

It is also known that the decomposition of ammonium nitrate is very much accelerated in presence of finely divided substances, *e.g.*, glass, graphite, spongy platinum, etc., and that gases other than ammonia and nitrous oxide are evolved. Reiset and Millon (*J. pr. Chem.*, 1843, **29**, 365) found that addition of platinum black caused evolution of nitrogen, ascribed by Berthelot to the reaction

$$5NH_4NO_3 \longrightarrow 4N_2 + 9H_2O + 2HNO_3 \quad . \quad . \quad . \quad (3)$$

In addition, the fused salt can decompose, evolving nitrogen peroxide or trioxide, nitrogen, and water :

$$4NH_4NO_3 \longrightarrow 3N_2 + N_2O_4 + 8H_2O \quad . \quad . \quad . \quad (4)$$

$$3NH_4NO_3 \longrightarrow 2N_2 + N_2O_3 + 6H_2O \quad . \quad . \quad . \quad (5)$$

If the salt be heated from 230° upwards, the decomposition becomes increasingly rapid and finally explosive, incandescence then setting in. According to Berthelot, the explosive reaction with the aid of a strong detonator is

$$2NH_4NO_3 \longrightarrow 2N_2 + 4H_2O + O_2 \quad . \quad . \quad . \quad (6)$$

and with the aid of a weak detonator

$$2NH_4NO_3 \longrightarrow N_2 + 4H_2O + 2NO \quad . \quad . \quad . \quad (7)$$

The latest work on the thermal decomposition of ammonium nitrate is that of Saunders (J., 1922, **121**, 698). From the results of gas analysis, he represented the main course of decomposition up to 260° by the equations (1) and (2) and also

$$5NH_3 + 3HNO_3 \longrightarrow 4N_2 + 9H_2O \quad . \quad . \quad . \quad (8)$$

The explosive decomposition was shown to proceed mainly according to

$$8NH_4NO_3 \longrightarrow 16H_2O + 2NO_2 + 4NO + 5N_2 \quad . \quad (9)$$

The equations (1) and (8) taken together yield equation (3), and equation (9) can be obtained from equations (4) and (7).

Veley and Saunders (*locc. cit.*) conducted their experiments under atmospheric pressure, using 100 g. and 40 g. of ammonium nitrate respectively. The former assumed that the gas evolved was nitrous oxide, which was measured by collecting the air displaced over saturated potassium sulphate solution. The free acid, which varied from 0·02 to 0·7%, was found to be nitric acid free from nitrous and hyponitrous acids, and was estimated by titration. Saunders did not examine the residue but drew his conclusions entirely from the composition of the gas evolved. Nitrous oxide was estimated by explosion with hydrogen, and nitric oxide and nitrogen peroxide by displacement of iodine from potassium iodide, nitrogen being found by difference. The gaseous products at all temperatures between 220° and 260° were almost constant, *i.e.*, 98% N_2O, 2% N_2, and 0·001% each NO and NO_2. The liquid products carried over with the gas contained nitrous and nitric acids and a little ammonium nitrate.

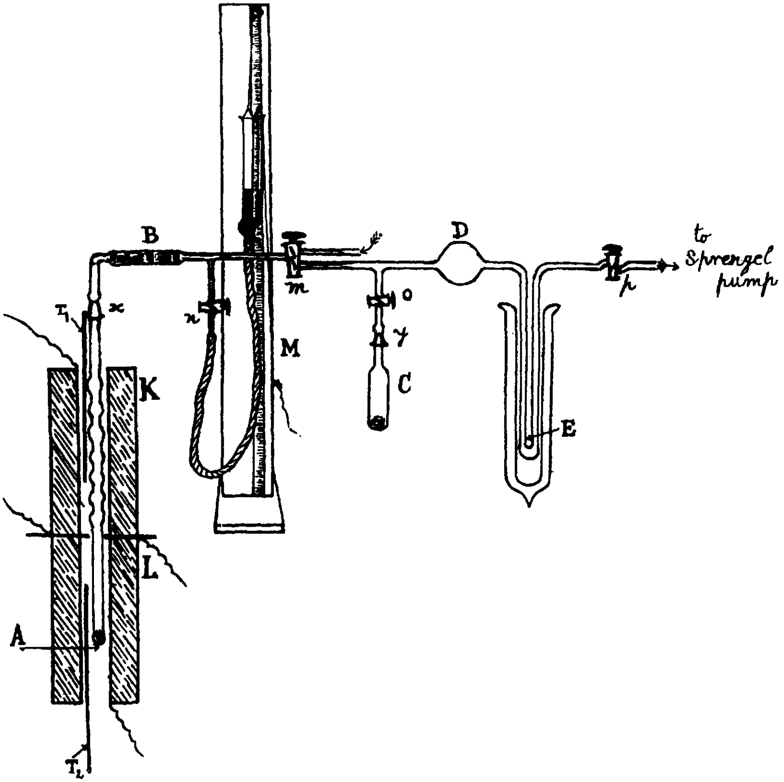
In the present investigation the decomposition has been studied by heating a constant quantity of ammonium nitrate (1 g.) in a vacuum and analysing quantitatively (*a*) the gas evolved and (*b*) the residue, the methods employed being more refined than those of the two foregoing workers. The recorded volumes of gases are reduced to N.T.P.

EXPERIMENTAL.

Method.—The construction of a suitable apparatus for studying the decomposition under vacuum presented difficulty : it was found, in agreement with Reik (*Monatsh.*, 1902, **23**, 1033), that ammonium nitrate when heated in a vacuum above its m. p. (169°) sublimes without undergoing decomposition. This difficulty was overcome by using two electric furnaces, the lower being maintained at the temperature of the experiment, and the upper one at 170°, *i.e.*, just above the m. p. The vapours of ammonium nitrate and of ammonia and nitric acid, which escape from the reaction chamber, tend to condense or recombine at the lower temperature of the upper furnace, and the liquid ammonium nitrate thus formed is returned to the reaction chamber. So long as the temperature of the upper furnace was kept between 165° and 175°, the rate of decomposition remained unaltered; there was a slight increase in the reaction velocity when the upper furnace was at 180° and a corresponding decrease when it was at 160°.

Procedure.—The apparatus is shown in Fig. 1. The column *A*, which contained a weighed quantity of pure dried ammonium nitrate, was connected by means of a ground-glass joint *x* to a three-way tap *m* through a six-inch layer of phosphoric oxide *B*. Before the commencement of each experiment a strip of paper containing mercurous nitrate was introduced in the apparatus above the ground joint *x* as a test for ammonia in the gas. The manometric connexion *M* with the tap *n* was used when required to read the pressure of the gas in the apparatus. On the other side of the tap *m*, one limb was attached to a bulb *C*, removable at the ground-glass joint *y* and containing moist sodium hydroxide, and also to a trap *E*. For increasing the dead space, a bulb *D* was inserted between *C* and *E*. Beyond *E* was the Sprengel pump. The connexion with the bulb *C* and the pump was secured whenever required by opening the taps *o* and *p* respectively.

Fig. 1.



After complete evacuation the apparatus was always tested for leaks by standing over-night. To begin the heating, the tap *m* was closed and the upper furnace *K* adjusted in the position shown in Fig. 1. The temperature was raised and maintained constant at 170°. The lower furnace, which was meanwhile heated on the bench to 1° or 2° above the temperature of the experiment, was then placed round the column *A* at a noted time. After the heating, both furnaces were removed, and the column *A* was allowed to cool. After the taps *o* and *p* had been closed, the trap *E* was immersed in liquid air and the tap *m* opened. Nitrous oxide and nitrogen peroxide and trioxide were condensed, leaving incondensable gas, which was collected by opening tap *p* and applying the pump; on analysis, this was found to contain only nitrogen.

The taps *m* and *p* were now closed, and the liquid air removed. Nitrogen peroxide or trioxide was detected by means of brown rings in the trap *E*. Whenever they were present, they were allowed to be absorbed by moist sodium hydroxide in *C* by opening the tap *o*. Nitrous oxide which remained in the gaseous state was pumped off and measured. The presence of nitrogen peroxide or trioxide was confirmed by detaching the bulb *C*, dissolving the solid in water, and testing the aqueous solution with acidified potassium permanganate or potassium iodide.

The tap *m* was finally left open to the air, and the column *A* removed from the ground joint *x*. The residue was dissolved in water, diluted to 250 c.c., and analysed. Ammonia was distilled off by displacement with sodium hydroxide, and absorbed in standard sulphuric acid; nitrate was determined by the ferrous sulphate method. Nitrate equivalent to the ammonia found was subtracted from the total nitrate: the difference gave the amount of free nitric acid present.

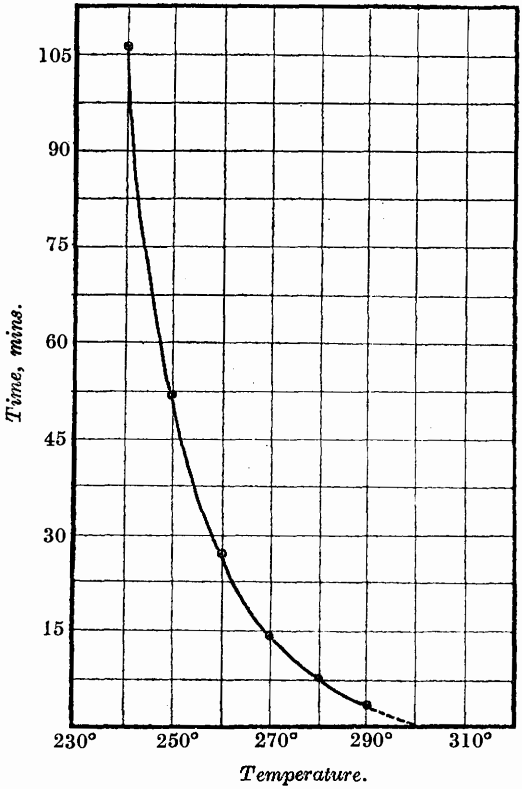
The solution was also tested for nitrous and hyponitrous acids by means of the sulphanilic acid–α-naphthylamine reaction. Negative results were obtained up to 270°: above that temperature a trace of nitrous acid was present.

Material.—The ammonium nitrate used was purified as follows. Merck's extra pure reagent was twice recrystallised from conductivity water, filtered, and left on porous tile in a sulphuric acid desiccator for four days. The middle portion of these crystals was put in a Pyrex beaker, which was kept in an air-oven at 120° for four days. The solid was then finely powdered and kept in a shallow vessel over phosphoric oxide under vacuum for one year. The product melted at 169°, in agreement with the m. p. of Early and Lowry (J., 1919, **115**, 1387) and of Saunders (*loc. cit.*) (Found: 0·987 g. gave 0·211 g. NH_3 and 0·777 g. NO_3. Calc.: 0·210 g. NH_3 and 0·765 g. NO_3).

Temperature of Decomposition.—Observations on the temperature at which ammonium nitrate begins to decompose differ widely; it is frequently given as about 280°, and Gmelin's "Handbuch" gives 250°. Pickering (*Chem. News*, 1878, **38**, 267) and Veley (*loc. cit.*) noted distinct evolution of gas at 185° and 186° respectively. We determined the temperature of decomposition in the following manner. The furnace *K* was maintained at 170°, and the effect on ammonium nitrate in column *A* of the rise in temperature of the furnace *L* was followed by observing the pressure of the evolved gas. At 185°, 190°, and 200°, ammonia was evolved as shown by the effect on mercurous nitrate paper. At 185° no increase in pressure was observed during 12 hours, and at 190° the pressure of the evolved gas in 3 hours was 9 mm., and at 200° 20 mm. of mercury. This shows that decomposition is perceptible at 190°.

Temperature and Rate of Decomposition.—An idea of the velocity of decomposition was first obtained by conducting experiments at various temperatures. The reaction was arrested when the pressure of the evolved gas was equal to one atmosphere, and the time required to reach this stage was noted. The evolved gas and the residue were then analysed. The results are given in Table I and the time–temperature curve is shown in Fig. 2.

FIG. 2.



These results show that (i) ammonia is evolved and free nitric acid accumulates in the residue; (ii) ammonium nitrate decomposes slowly at 240° and rapidly at 290°, the rate of decomposition being

TABLE I.

Temp.	Time (mins.).	Gas evolved, c.c.		Residue, g.		
		N_2.	N_2O.	NH_3.	HNO_3.	Free HNO_3
240°	107	1·1	34·3	0·1704	0·6807	0·0492
250	52	1·1	34·2	0·1693	0·6730	0·0456
260	27	1·1	33·0	0·1653	0·6701	0·0575
270	14	1·2	33·7	0·1704	0·6796	0·0481
280	8	1·0	31·8	0·1704	0·6823	0·0508
290	3·5	1·0	31·7	—	—	—
300		The decomposition is violent.				

approximately doubled by each rise of 10° : the decomposition is violent at 300°, as stated by Saunders (*loc. cit.*); (iii) over the range 240—290° the main products of decomposition are nitrous oxide and water : nitrogen also is formed, the ratio N_2/N_2O remaining almost constant.

Effect of Pressure.—The effect of pressure on the decomposition of ammonium nitrate was next studied. The furnace *L* was maintained at 240°, and the decomposition was allowed to proceed till the pressure of the gas evolved was 10, 16, 26 . . . 76 cm. of mercury. The composition of the evolved gas and of the residual mass is given in Table II. Fig. 3 represents the curve obtained by plotting the volume of nitrous oxide against pressure.

TABLE II.

Pressure, cm. Hg.	Time, mins.	Gas evolved, c.c.		Residue, g.		
		N_2.	N_2O.	NH_3.	HNO_3.	Free HNO_3.
10	14	0·6	4·3	—	—	—
16	23	0·6	7·3	—	—	—
26	37	0·6	11·9	0·183	0·744	0·0657
36	51	0·6	16·8	0·176	0·714	0·0620
46	65	0·7	22·0	—	—	—
56	80	0·8	27·5	0·175	0·709	0·0606
66	94	1·0	31·9	0·175	0·694	0·0456
76	108	1·2	36·6	0·169	0·663	0·0367

These results show that (i) ammonia escapes before the decomposition (other than dissociation) starts, and free nitric acid accumulates in the residue; (ii) the amount of nitrous oxide is directly proportional to the pressure : in unit time the amount produced is not greater at a low than at a high pressure; (iii) the ratio N_2/N_2O tends to be high at a low pressure.

Effect of Mass.—From the foregoing experiments it would appear that the three main reactions involved in the decomposition of ammonium nitrate are (*a*) dissociation into ammonia and nitric acid; (*b*) production of nitrogen; (*c*) decomposition into nitrous oxide and water. Since a low pressure should favour reaction (*a*) and the vaporisation of the products, and is found to favour the production of nitrogen, it is probable that the last arises by the interaction of the ammonia and nitric acid in the gaseous state. The formation of nitrous oxide, on the other hand, may be due to the decomposition of ammonium nitrate either in the gaseous or in the liquid state. The decomposition was therefore studied of different amounts of ammonium nitrate at 240°; in all cases it was stopped after 45 minutes, the gaseous products and the residue being analysed. The results are given in Table III, and the composition of the evolved gas is shown in Fig. 4.

FIG. 3.

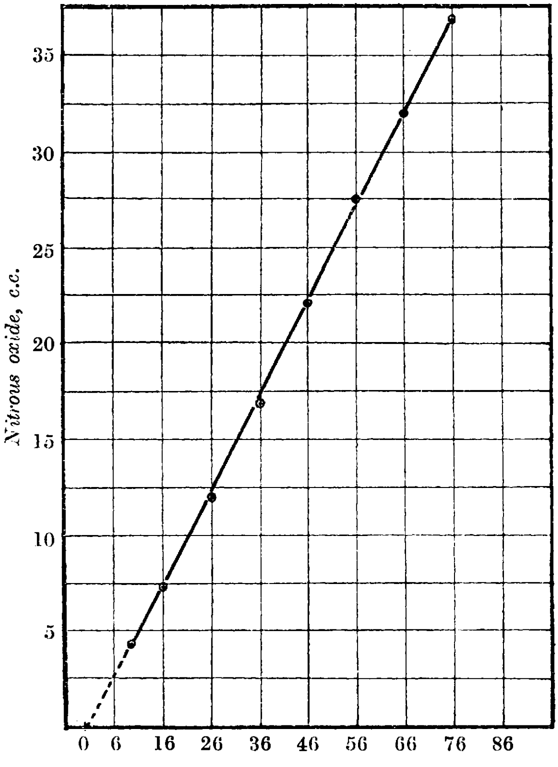
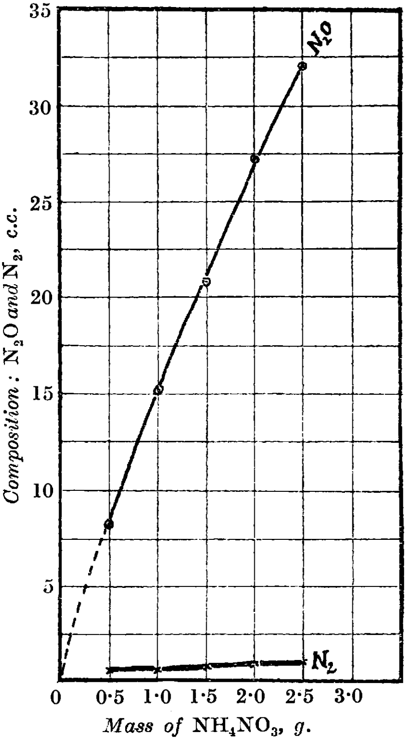


TABLE III.

NH_4NO_3, g.	Gas evolved, c.c. N_2.	Gas evolved, c.c. N_2O.	Residue, g. NH_3.	Residue, g. HNO_3.	Residue, g. Free HNO_3.
0·5	0·6	8·4	0·0882	0·3444	0·0176
1·0	0·6	15·3	0·1776	0·7213	0·0630
1·5	0·9	20·8	0·2694	1·1307	0·1321
2·0	1·0	27·2	0·3633	1·4987	0·1527
2·5	1·1	31·9	0·4570	1·8704	0·1774

These results show that (i) ammonia is evolved; (ii) the free nitric acid accumulating in the residue increases as the amount of ammonium nitrate increases; (iii) nitrogen is produced, its proportion being greater when the pressure is low and when the amount of ammonium nitrate is small: since a low pressure favours the dissociation and a small amount of ammonium nitrate favours the production of nitric acid as vapour, it seems that the nitrogen is formed by the interaction of ammonia and nitric acid in the gaseous phase; (iv) apart from water, the principal product in the decomposition of ammonium nitrate is nitrous oxide, the ratio of the two being constant, so it appears that the nitrous oxide is formed by the decomposition of ammonium nitrate, not in the gaseous, but in the liquid phase.

FIG. 4.



Influence of Foreign Substances.—Saunders (*loc. cit.*) studied the effect of small quantities of commonly occurring impurities in ammonium nitrate, and noted that chlorides have a marked effect on its rate of decomposition, sulphates and nitrates being without any characteristic action.

With a view to test the validity of the conclusions (iii) and (iv) above, the influence of (1) thoria, (2) anhydrous sodium sulphate, (3) anhydrous arsenic acid, and (4) anhydrous copper sulphate was investigated. The last three were obtained from Merck, and the first from Kahlbaum. Before use, these substances were left in the desiccator over phosphoric oxide for one year. Experiments were conducted with 1·0 g. of ammonium nitrate in absence and in presence of 0·1 g. of each of these substances, and also with 0·5 g. of (1), (2), and (4). The apparatus and procedure were practically the same as described above: the reaction was allowed to proceed at various temperatures for 20 minutes, and the evolved gas and the residue were analysed. In experiments with arsenic acid and copper sulphate, however, the manometric connexion *M* was excluded by closing the tap *n*, because in preliminary experiments it was noticed that the mercury in the manometer was attacked by nitrogen peroxide, nitrous anhydride being evolved. The results of gas analysis are given in Table IV. The general nature of the residue is shown by the results at 250° (Table V).

TABLE IV.

Decomposition of 1·0 *g. of ammonium nitrate in presence of other substances.*

	(Alone).			As_2O_5 (0·1 g.).			ThO_2.					
							0·1 g.			0·5 g.		
Temp.	N_2, c.c.	N_2O, c.c.	N_2, %.	N_2, c.c.	N_2O, c.c.	N_2, %.	N_2, c.c.	N_2O, c.c.	N_2, %.	N_2, c.c.	N_2O, c.c.	N_2, %.
220°	—	—	—	0·3	8·3	3·5	—	—	—	—	—	—
230	0·4	4·7	7·8	0·6	13·0	4·4	0·5	4·0	11·1	1·1	5·7	16·2
240	0·7	7·4	8·8	trace	22·6	—	·06	6·9	8·0	0·8	10·3	7·2
250	0·8	13·7	5·5	0·8	41·8	1·9	trace	13·0	—	0·6	20·1	2·9
260	1·1	29·2	3·6	1·5*	63·9*	2·3*	0·6	27·1	2·1	0·8	47·0	1·7
270	1·0	47·5	2·1	—	—	—	0·8	43·8	1·8	—	—	—

	Na_2SO_4.						$CuSO_4$.					
	0·1 g.			0·5 g.			0·1 g.			0·5 g.		
210	—	—	—	—	—	—	2·0	4·2	32·2	—	—	—
220	—	—	—	—	—	—	1·8	5·2	25·7	2·7	7·5	26·4
230	trace	5·2	—	0·6	6·3	8·7	2·7	9·8	21·6	3·4	12·4	21·5
240	0·4	11·1	3·4	0·8	12·8	5·9	2·9	17·6	14·1	5·5	29·7	15·6
250	trace	20·2	—	1·0	33·7	2·9	2·8	29·0	8·8	7·5	76·3	8·9
260	1·0	44·0	2·2	Decomposition			—	—	—	—	—	—
270	1·2	69·3	1·7	very rapid			—	—	—	—	—	—

Remarks.—As_2O_5. No NH_3 evolved; much free HNO_3 present; NO_2 and NO also evolved.†
ThO_2. NH_3 evolved in quantity; free HNO_3 absent from residue.
Na_2SO_4. NH_3 evolved; free HNO_3 in residue.
$CuSO_4$. NH_3 evolved; much free HNO_3 present; NO_2 and NO also evolved, but less than with As_2O_5.†

* This experiment was checked after 10 minutes, and the results of gas analysis are doubled.
† Oxygen was tested for and found to be absent in all these experiments.

TABLE V.

	Residue, g.			
Experiments with 0·1 g. of	NH_3.	HNO_3.	Free HNO_3.	Remarks.
(Alone)	0·1681	0·6749	0·0521	
Thoria	0·1621	0·5980	—	Free acid absent.
Na_2SO_4	0·1780	0·6988	0·0394	Free acid decreases.
As_2O_5	0·1468	0·6203	0·0751	Free acid increases.
$CuSO_4$	0·1537	0·6680	0·0990	,, ,, ,,

The four substances used in admixture were selected because it was thought that the reactions, *viz.*, (*a*) dissociation, (*b*) production of nitrogen owing to oxidation of ammonia by nitric acid in the gaseous phase, and (*c*) formation of nitrous oxide by the decomposition of liquid ammonium nitrate, would be affected in the following manner. Thoria, being basic, was expected to increase the concentration of ammonia and diminish that of nitric acid, thereby inhibiting reaction (*b*). Sodium sulphate would tend to retard (*a*) and hence diminish (*b*). Arsenic acid would decrease the concentration of ammonia and increase that of nitric acid, thus retarding (*b*). Copper sulphate would affect (*a*) and (*b*) in the same way as sodium sulphate. Further, it was expected that, once the hydrate is formed, it would show the behaviour (i) of a feeble acid and (ii) of complex formation with ammonia; (i) would lead to an increase in the concentration of nitric acid, and (ii) would lead to an increase or a decrease in the concentration of ammonia according to the stability of the complex formed.

Moreover, the presence of any of these substances in liquid ammonium nitrate would tend to accelerate reaction (*c*).

The results in Tables IV and V show that these expectations are fulfilled. In addition, it is seen that (i) some nitrogen peroxide or trioxide is evolved in experiments with arsenic acid and copper sulphate, its amount being greater in the former case; (ii) in all the experiments, nitrous oxide is the principal product of the decomposition and its production is accelerated by all the added substances; (iii) the ratio N_2/N_2O is the same for experiments with 0·1 g. as for 0·5 g. of copper sulphate; with thoria and sodium sulphate, the quantity added affects this ratio.

Discussion of Results.

The indication of all observations recorded above on the mechanism of decomposition of ammonium nitrate is that it first dissociates according to equation (1). Some ammonia always escapes initially owing to its higher rate of diffusion, leaving free nitric acid which is invariably found in the residual mass. The amount of ammonia evolved increases, and that of nitric acid formed decreases, when a basic substance is present, and *vice versa* when an acid substance is used.

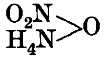
That ammonia and nitric acid react in the gaseous state producing nitrogen according to Saunders's equation (8) is shown by the facts that the proportion of nitrogen evolved is (1) increased by use of low pressure or small quantities, and is (2) diminished when (*a*) dissociation is retarded by the presence of a neutral anhydrous substance (sodium sulphate), (*b*) the concentration of ammonia is increased and that of nitric acid simultaneously diminished by addition of a basic substance (thoria), and (*c*) the concentrations are altered in the opposite sense by addition of an acid substance (arsenic acid). The amount of nitrogen evolved in the copper sulphate experiments is greater than that produced in other experiments for the reasons adumbrated above.

The oxidation of ammonia by nitric acid according to (8) evidently adds to the content of the free nitric acid in the residual mass. When this concentration is fairly high, as in experiments with arsenic acid and copper sulphate, nitric oxide and nitrogen peroxide are evolved. The formation of these oxides, in absence of oxygen, shows that the formation of nitrogen, represented by a direct reaction in (8), is more likely to proceed in stages, the sum of which is identical with (8) :

$$NH_3 + 3HNO_3 = (N_4O_6 + 3H_2O) = 4HNO_2 + H_2O \quad . \quad (10)$$

$$4NH_3 + 4HNO_2 = (4NH_4NO_2) \quad = 4N_2 + 8H_2O \quad . \quad . \quad (11)$$

The reaction (10), and hence (11), is inhibited by the fall in concentration of nitric acid, *e.g.*, in experiments with thoria, and both reactions (the latter in particular) are affected by the fall in concentration of ammonia, *e.g.*, in experiments with arsenic acid. This also explains the formation of nitrous acid, which is detected in the residue in experiments above 270°.

The principal product of the decomposition of ammonium nitrate in all these experiments is nitrous oxide (along with water). The facts that the proportion of nitrous oxide produced in unit time is not greater at low than at high pressures, that it increases as the mass of ammonium nitrate is increased, and that its production is accelerated in presence of foreign substances show that molten ammonium nitrate is likely to undergo decomposition according to equation (2). Such an evolution of nitrous oxide is in agreement with what might be expected from Divers's "oxylic" constitution  $\begin{matrix} O_2N \\ H_4N \end{matrix}\!\!>\!O$ of ammonium nitrate (J., 1885, **47**, 232).

In view of the effect of heat on the nitrates of alkali metals, one might expect ammonium nitrate to decompose first into ammonium nitrite and oxygen, the former yielding nitrogen and water vapour. That this does not occur is shown by the absence of oxygen from the evolved gases, and of ammonium nitrite from the residue in experiments below 270°. The other possibility, that nitrogen may be evolved by the thermal decomposition of nitrous oxide produced in the experiment, is also untenable because this occurs only above 500° in absence of catalysts and above 280° in their presence (Shah, J., 1929, 2678).

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