

HETEROGENEOUS CHEMICAL REACTIONS IN THE  
SILENT ELECTRIC DISCHARGE. VII.

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Investigations of the reduction of a number of inorganic solid substances by hydrogen in the silent electric discharge have been carried out over a considerable period; there follows an account of the results obtained since the publication of the previous papers.<sup>(1)</sup>

The apparatus and method of investigation are the same as those previously mentioned.<sup>(1)</sup>

## Experimental.

(1) **Lithium Nitrate.** A gas absorption apparatus similar to that employed in the case of calcium nitrate<sup>(2)</sup> was connected to the apparatus. Nitrogen peroxide contained in the gaseous reaction products is absorbed by alkaline solution in absorption bottle (1), nitric oxide is then oxidized by air and absorbed by alkaline solution in absorption bottle (2), and, lastly, ammonia gas is absorbed by dilute sulphuric acid solution in absorption bottle (3).

Exp. 1. A qualitative experiment was first carried out.

The quantity of lithium nitrate,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Water was produced during the reaction and part of the powder in the discharge tube became moist.

Distilled water was added into the discharge tube and the chemical properties of the solution produced were examined, with the following results:—

- (a) The solution was basic. It coloured red litmus paper blue.
- (b) On adding silver nitrate solution, a chocolate-brown precipitate of silver oxide was produced.
- (c) The solution was neutralized with nitric acid solution and silver nitrate solution added. No yellow precipitate was obtained, proving the absence of hyponitrite.

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(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202.

(2) S. Miyamoto, *ibid.*, **54** (1933), 89.

- (d) The solution was added to Fehling's solution and heated. No reduction took place, proving the absence of hydroxylamine.
- (e) The solution was placed in a test tube, potassium iodide solution added, acidified with dilute sulphuric acid solution and a few drops of starch solution added. The solution was coloured blue, proving the presence of nitrite.
- (f) The solution was placed in a test tube and heated. Moist red litmus paper became blue, proving the evolution of ammonia.

The alkaline solution in absorption bottle (1) was placed in a test tube, potassium iodide solution added, acidified with dilute sulphuric acid solution and a few drops of starch solution added. The solution was coloured slightly blue, proving that a minute quantity of nitrogen peroxide had been produced during the reaction.

By analyzing the alkaline solution in absorption bottle (2) it was proved that nitric oxide is not a gaseous reaction product.

The sulphuric acid solution in absorption bottle (3) was placed in a test tube, alkalinized with sodium hydroxide solution and heated. The evolution of ammonia gas was proved.

Exp. 2. The solid reaction product was dissolved in water and the total volume of the solution was made up to 100 c.c. The quantity of nitrite was determined in the normal manner.

Lithium nitrate employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.10 c.c.

Exp. 3. The solid reaction product was dissolved in dilute nitric acid solution, and distilled with an excess of sodium hydroxide solution. The ammonia gas evolved was absorbed by a definite quantity of sulphuric acid solution. The distillation was stopped when no further evolution of ammonia took place, and the excess of sulphuric acid was titrated with sodium carbonate solution.

The quantity of ammonia gas absorbed by sulphuric acid solution in absorption bottle (3) during the reaction was similarly determined.

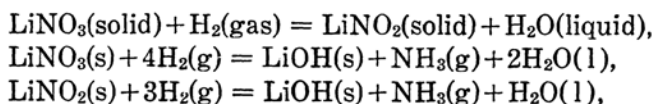
Lithium nitrate employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia evolved when the solid reaction product was distilled with an excess of sodium hydroxide solution = 0.24 c.c.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed by sulphuric acid solution in absorption bottle (3) = 0.29 c.c.

From these experimental facts, it would seem that the principal chemical reactions in the discharge tube are expressed by the following equations.



(2) **Beryllium Nitrate.** Exp. 1. The quantity of beryllium nitrate,  $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , employed = 8.00 gr. Time of silent electric discharge = 5 hours.

A gas absorption apparatus similar to that employed in the previous case was connected to the discharge tube.

Soon after the electric current was passed, a considerable quantity of brown coloured gas, which is undoubtedly nitrogen peroxide, evolved in the discharge tube. Water was found condensed on the wall of the discharge tube.

Water was poured into the discharge tube, well shaken and filtered. A small quantity of insoluble white powder remained. It was filtered and washed. The insoluble white powder is undoubtedly beryllium hydroxide. The filtrate had the following chemical properties.

- (a) The solution was acidic. This is due to the hydrolysis of beryllium nitrate unchanged.
- (b) By the identical method employed in the previous case, it was proved that the solution contained nitrite. As beryllium nitrite is unknown, the nitrite contained in the solution is supposed to be ammonium nitrite produced during the reaction.
- (c) The presence of ammonium salt was proved.
- (d) The absence of hydroxylamine was proved in the normal manner.

Exactly as in the case of lithium nitrate, it was proved that the gaseous reaction products contained no ammonia gas but considerable quantities of nitrogen peroxide and nitric oxide.

Exp. 2. The quantity of ammonium salt produced was determined in the normal manner.<sup>(3)</sup>

Beryllium nitrate employed = 8.00 gr.

Time of silent electric discharge = 5.5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 8.47 c.c.

Exp. 3. The quantities of nitrite, nitrogen peroxide and nitric oxide produced were determined.

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(3) Treadwell, "Kurztes Lehrbuch der analytischen Chemie," 10. Aufl., 2. Bd., S. 483.

On leaving the discharge tube, the gas was first passed through two absorption bottles containing sodium hydroxide solution (a), the gas was then mixed with a sufficient quantity of air and passed through two absorption bottles containing sodium hydroxide solution (b).

The quantity of nitrite contained in the solid reaction products was determined in the normal manner.

Beryllium nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

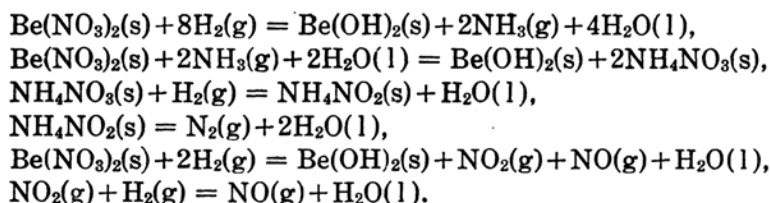
Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced in the solid phase = 2.80 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottle (a) formed by absorbing nitrogen peroxide = 249.40 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottle (b) formed by absorbing nitrogen peroxide, which is the oxidation product of nitric oxide, produced during the reaction = 522.20 c.c.

From these experimental facts, it is certain that the principal reaction products are beryllium hydroxide, nitrite, ammonium salt, nitrogen peroxide and nitric oxide. It is a notable fact that the quantities of nitrogen peroxide and nitric oxide produced in this case are considerable compared with those produced in the case of nitrates of other metals, such as magnesium,<sup>(4)</sup> zinc,<sup>(5)</sup> cadmium,<sup>(6)</sup> calcium,<sup>(7)</sup> strontium<sup>(8)</sup> and barium.<sup>(9)</sup>

It is probable that the principal chemical reactions in the discharge tube are expressed by the following equations.



(3) **Mercuric Nitrate.** The investigation of the reduction of mercuric nitrate was repeated to supplement the previous study.<sup>(10)</sup>

Exp. 1. The quantity of mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , employed = 8.00 gr.  
Time of silent electric discharge = 6 hours.

(4) S. Miyamoto, *J. Chem. Soc. Japan*, **54** (1933), 209.

(5) *Ibid.*, **54** (1933), 210. (6) *Ibid.*, **54** (1933), 211.

(7) *Ibid.*, **54** (1933), 89. (8) *Ibid.*, **54** (1933), 91.

(9) *Ibid.*, **54** (1933), 92. (10) *Ibid.*, **53** (1932), 942.

A gas absorption apparatus similar to that employed in the case of lithium nitrate was connected to the discharge tube.

Virtually no change was observed in the appearance of the powder in the discharge tube.

The solid reaction product was first examined and it was proved that it contained no explosive compounds. The solid reaction product was then shaken with water and filtered. An insoluble yellow powder remained, which is undoubtedly mercuric oxide. The filtrate had the following properties.

- (a) The solution was acidic.
- (b) A sufficient quantity of sodium hydroxide solution was added to the solution and the precipitated mercury oxide filtered. The filtrate contained no hydroxylamine.
- (c) The solution contained nitrite. The quantity of nitrite produced was determined in the previous study.<sup>(10)</sup>
- (d) Exactly as in the case of beryllium nitrate, it was proved that the solution contained a considerable quantity of ammonium salt.
- (e) It was proved that the solution contained mercurous salt. The quantity of mercurous salt produced was determined in the previous study.<sup>(10)</sup>

Exactly as in the case of lithium nitrate it was proved that the gaseous reaction products contained neither ammonia nor nitric oxide, but nitrogen peroxide.

The quantity of nitrogen peroxide produced was determined in the previous experiment.<sup>(10)</sup>

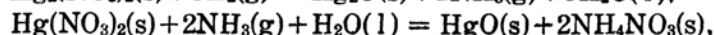
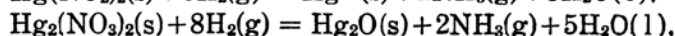
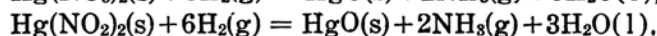
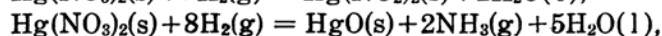
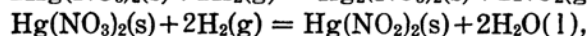
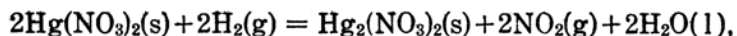
Exp. 2. The solid reaction products were dissolved in dilute nitric acid solution and the quantity of ammonium salt was determined in the normal manner.

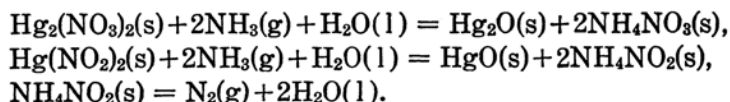
Mercuric nitrate employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 12.13 c.c.

From these experimental facts it would seem that the principal chemical reactions in the discharge tube are expressed by the following equations.





(4) **Mercurous Nitrate.** This investigation of the reduction of mercurous nitrate was carried out to supplement the previous study.<sup>(11)</sup>

Exp. 1. The quantity of mercurous nitrate,  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , employed = 8.00 gr.  
Time of silent electric discharge = 5 hours.

The white powder in the discharge tube became grey in colour. The solid reaction products were shaken with water. An insoluble white powder and small drops of metallic mercury remained. The quantity of metallic mercury was determined in the previous study. The solution had the following chemical properties.

- (a) The solution was acidic.
- (b) The solution contained ammonium salt.
- (c) The solution contained nitrite. The quantity of the produced nitrite was determined in the previous study.
- (d) Sodium hydroxide was added to the solution and the precipitated mercury oxide filtered. The absence of hydroxylamine in the filtrate was proved.

By analyzing the alkaline solutions in absorption bottles (1) and (2) it was proved that nitrogen peroxide and a minute quantity of nitric oxide had been produced during the reaction.

By analyzing the sulphuric acid solution in absorption bottle (3) it was proved that the gaseous reaction products contained no ammonia.

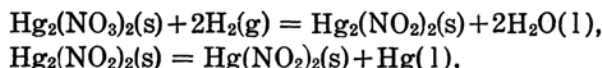
Exp. 2. The production of ammonium salt was studied quantitatively. The solid reaction products were well shaken with dilute nitric acid solution, and the drops of metallic mercury were separated by decantation. The quantity of ammonium salt contained in the solution was determined in the normal manner.

Mercurous nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

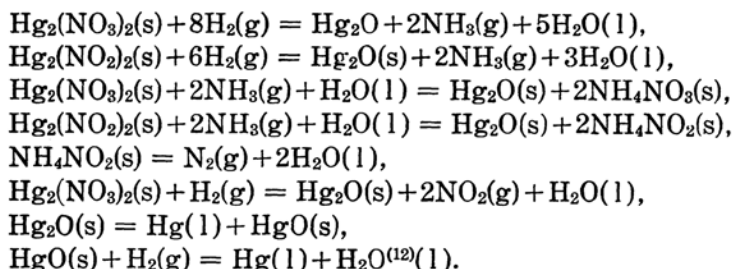
Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 9.48 c.c.

From these results the principal reactions in the discharge tube are considered to be those expressed by the following equations.




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(11) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 943.



(5) **Lead Nitrate.** Exp. 1. The quantity of lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , employed = 8.00 gr. Time of silent electric discharge = 5 hours.

A gas absorption apparatus similar to that employed in the previous experiment was connected to the discharge tube. A part of the white powder in the discharge tube became black. It was first proved that the solid reaction product did not contain any explosive compound. The powder was then shaken with water and filtered. A small quantity of white powder mixed with a minute quantity of black powder remained. It is certain that the insoluble substance is a mixture of lead hydroxide and metallic lead. The filtrate had the following properties.

- (a) The solution coloured red litmus paper slightly blue.
- (b) Sodium carbonate solution was added to the solution and the precipitated lead carbonate filtered. The absence of hydroxylamine in the filtrate was proved.
- (c) The presence of nitrite in the solution was proved.
- (d) The solution contained ammonium salt.

It was proved that the gaseous reaction products contained a small quantity of nitrogen peroxide and ammonia, but no nitric oxide.

Exp. 2. The formation of nitrite was studied quantitatively.

Lead nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 3.80 c.c.

Exp. 3. The quantity of ammonium salt contained in the solid reaction product was determined.

Lead nitrate employed = 8.00 gr.

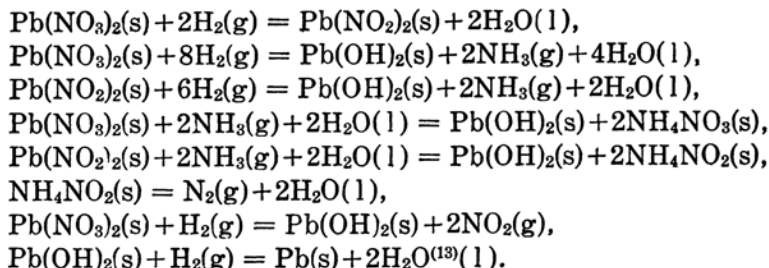
Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 0.85 c.c.

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(12) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 793.

From these experimental facts, it would seem that the principal reactions are expressed by the following equations.



(6) **Bismuth Nitrate.** Exp. 1. The quantity of bismuth nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , employed = 8.00 gr. Time of silent electric discharge = 5 hours.

Soon after the electric current had been passed, a considerable quantity of brown coloured gas, undoubtedly nitrogen peroxide, evolved in the discharge tube. A part of the powder in the discharge tube became black. A minute quantity of metallic bismuth must have been produced. The solid reaction product was shaken with water. A small quantity of insoluble white substance remained: this is undoubtedly bismuth hydroxide. The insoluble matter was filtered. The filtrate had the following properties.

- (a) The solution was acidic.
- (b) The solution contained ammonium salt.
- (c) The presence of nitrite was proved.
- (d) It was proved that the solution contained no hydroxylamine.

By analyzing the solutions in absorption bottles (1), (2) and (3), it was proved that the gaseous reaction products contained nitrogen peroxide and nitric oxide, but no ammonia gas.

Exp. 2. The quantities of nitrite, nitrogen peroxide and nitric oxide produced were determined by the method employed in the case of beryllium nitrate.

Bismuth nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.0100 normal, equivalent to the quantity of nitrite produced in the solid phase = 5.45 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottles (1), produced by absorbing nitrogen peroxide = 569.80 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottles (2), produced by absorb-

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(13) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 794.



ing nitrogen peroxide, the oxidation product of nitric oxide, a gaseous reaction product = 811.30 c.c.

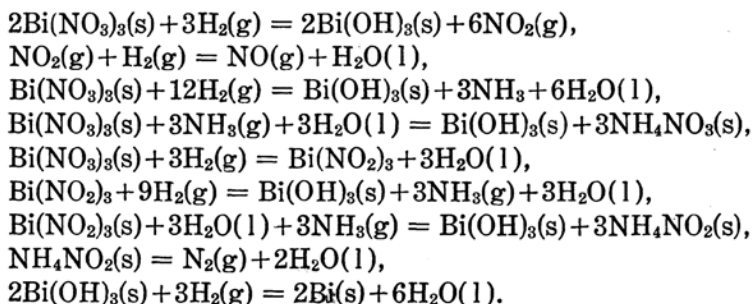
Exp. 3. The quantity of ammonium salt produced was determined.

Bismuth nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 1.88 c.c.

From these experimental facts, it would seem that the principal chemical reactions are expressed by the following equations.



As in the case of beryllium nitrate, the quantities of nitrogen peroxide and nitric oxide contained in the gaseous reaction products were considerable.

(7) **Aluminium Nitrate.** Exp. 1. The quantity of aluminium nitrate,

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , employed = 8.00 gr. Time of silent electric discharge = 5 hours.

The powder in the discharge tube became moist owing to the formation of water by the reduction. Distilled water was poured into the discharge tube, well shaken, and filtered. A minute quantity of white powder remained. The powder was placed in a test tube, dilute hydrochloric acid solution added and warmed. It dissolved, forming aluminium chloride solution. It is therefore certain that the white powder, insoluble in water, is aluminium oxide. The filtrate had the following properties.

- (a) The solution was acidic. This is due to the presence of unchanged aluminium nitrate.
- (b) It was proved that the solution contained nitrite. As aluminium nitrite is unknown, it would seem that the produced nitrite must be ammonium nitrite, formed by the reaction.
- (c) The solution contained ammonium salt.
- (d) The solution contained no hydroxylamine.

By a method similar to that employed in the case of lithium nitrate it was proved that the gaseous reaction products contained neither nitric oxide nor ammonia gas, but nitrogen peroxide.

Exp. 2. A second experiment was carried out to determine the quantity of ammonium salt produced.

Aluminium nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 10.34 c.c.

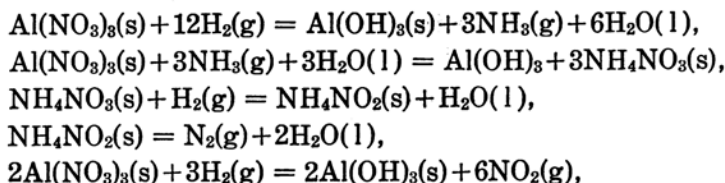
Exp. 3. The quantity of nitrite, contained in the solid reaction products, was determined in the normal manner.

Aluminium nitrate employed = 8.00 gr.

Time of silent electric discharge = 4.5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.15 c.c.

From these experimentally obtained facts it follows that the principal reaction products are ammonium salt, aluminium hydroxide, nitrite and nitrogen peroxide, and it would seem that the chemical reactions are expressed by the following equations.



(8) **Ammonium Nitrate.** Exp. 1. The quantity of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , employed = 8.00 gr. Time of silent electric discharge = 5 hours.

A gas absorption apparatus, similar to that employed in the previous experiment was connected to the discharge tube. Virtually no change was observed in the appearance of the powder in the discharge tube. The solid reaction products were dissolved in water. The solution had the following properties.

- (a) The solution was neutral.
- (b) The solution contained no hydroxylamine.
- (c) The solution contained a minute quantity of nitrite.

It was proved that the gaseous reaction products contained ammonia and a minute quantity of nitrogen peroxide, but no nitric oxide.

Exp. 2. The nitrite and the ammonia gas produced were determined quantitatively.

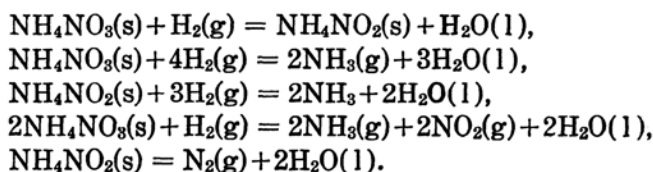
Ammonium nitrite employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 0.10 c.c.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia gas evolved = 0.29 c.c.

From these experimental facts it would seem that the chemical reactions are those expressed by the following equations.



The writer wishes to express his appreciation of a grant from the Imperial Academy towards the expences of this research.

### Summary.

The chemical reactions in the silent electric discharge were studied when hydrogen reacts on the following inorganic solid substances.

(1) Lithium nitrate. Reaction products:—lithium hydroxide, nitrite, ammonia and nitrogen peroxide.

(2) Beryllium nitrate. Reaction products:—beryllium hydroxide, ammonium salt, nitrite, nitrogen peroxide and nitric oxide.

(3) Mercuric nitrate. Reaction products:—mercury oxide, mercurous salt, ammonium salt, nitrite and nitrogen peroxide.

(4) Mercurous nitrate. Reaction products:—mercury oxide, metallic mercury, ammonium salt, nitrite, nitrogen peroxide and nitric oxide.

(5) Lead nitrate. Reaction products:—lead hydroxide, ammonium salt, nitrite, (metallic lead), nitrogen peroxide and ammonia.

(6) Bismuth nitrate. Reaction products:—bismuth hydroxide, ammonium salt, nitrite, (metallic bismuth), nitrogen peroxide and nitric oxide.

(7) Aluminium nitrate. Reaction products:—aluminium oxide, ammonium salt, nitrite and nitrogen peroxide.

(8) Ammonium nitrate. Reaction products:—nitrite, ammonia and nitrogen peroxide.

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