ranged in distinct layers. Rarely were the gaps between these bands free from crystals.

Liesegang[1] insists that silver chromate bands in gelatin only when definite small quantities of acid are present. The great field opened by the use of basic gels leaves to this observation a rather limited application.

Davis,[2] in securing bands of colloidal mercury, argues that there must have been supersaturation with this same colloid. In this connection my experiments with bands of colloidal gold might be studied. Throughout the red-blue-green bands of colloidal gold and the gaps as well were countless, gleaming, yellow crystals of gold.

Liesegang's "dead space" experiment[3] confirms the theory advanced in this paper. He filled a glass tube (open at both ends) with gelatin containing 10% of sodium chloride. This tube was then immersed in a solution of silver nitrate which diffused into the gel from both ends of the tube precipitating silver chloride in two bands. However, these two bands of silver chloride did not meet in the middle of the tube. A clear dead space remaining in the center of the tube contained no sodium chloride at all. The salt originally there had diffused away in opposite directions. A dead space was not formed when a gel containing a non-diffusing substance such as albumin was immersed in metaphosphoric acid.

Those who do not accept the theory I have advanced will, at least, find in the experimental evidence new and superior methods for investigating the problem.

OBERLIN, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

THERMAL DECOMPOSITION OF CERTAIN INORGANIC TRINITRIDES.

BY ARTHUR R. HITCH.

Received May 16, 1918.

Anticipating a later investigation of the atomic weight of nitrogen, and searching for a more satisfactory method than the proposed electrolysis of silver trinitride in anhydrous liquid ammonia, the author conceived the idea that it might be possible to decompose silver trinitride smoothly by subjecting it to constant heat for some time, just below the exploding point of the compound. Preliminary experiments along this line gave such promising results that it was considered more important to proceed with the study of a number of other inorganic trinitrides,

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[1] *Z. phys. Chem.*, **88**, 1 (1914).

[2] THIS JOURNAL, **39**, 1312 (1917).

[3] *Z. angew. Chem.*, **23**, 2124 (1910).

namely, mercurous, mercuric, barium, thallous, lead, copper, ammonium, sodium, and potassium trinitrides, in a similar manner, deferring the work on the atomic weight of nitrogen to some future date.

As far as can be ascertained from the literature, practically no work has ever been done upon the slow decomposition at high temperatures of any of the trinitrides. Many of the trinitrides studied in this investigation, for example, silver, mercurous, mercuric, lead, cupric, and thallous trinitrides, act like so-called fulminates, in that they explode violently when sharply struck, by friction with substances like powdered glass, or if touched with a glowing body. Some will explode even on breaking the crystals. It was found that mercuric trinitride was particularly sensitive in this respect, exploding even as it crystallizes out from solution, especially when prepared by precipitating from a solution of mercuric nitrate with sodium trinitride. Unlike mercury fulminate, silver fulminate or the acetylides, the trinitrides appear to be just as sensitive in the wet as in the dry state. Ammonium, sodium, potassium, and barium trinitrides will not explode when struck, or by friction, even with substances like powdered glass, but will explode with a slight puff when quickly heated or when touched with a glowing body.

The trinitrides studied in this investigation are all well-defined, crystalline, and comparatively stable compounds at ordinary temperatures, but many are quite easily affected by sunlight, with evolution of nitrogen, the author's observations confirming most of those made by L. Wöhler.[1] Silver trinitride became violet, then gray, and finally black; lead trinitride yellowish brown, dark brown and finally nearly black; cupric trinitride brown at first and on exposure a dark brown; mercurous trinitride yellow, orange, brown and dark brown; mercuric trinitride was formed as clear, long, needle-like crystals which became slightly yellowish on exposure to sunlight, but which evolved nitrogen more rapidly than any of the other salts observed. The partly decomposed substances show practically the same sensitiveness to explosion as the original salts.

Silver Trinitride.

Preparation.—This compound was first described by Curtius.[2] For this investigation the salt was prepared by treating in the cold a 4% aqueous solution of silver nitrate with a slight excess of a 4% aqueous solution of hydronitric acid made by the distillation of 96% sodium trinitride (obtained from F. Raschig, Ludwigshafen) with 6 *N* sulfuric acid. The resulting white precipitate which came down quantitatively was quickly washed free from all hydronitric acid, dried in a dark air bath at 110° for 3 hours, and then placed in a dark glass vacuum desiccator over conc. sulfuric acid. Silver trinitride, if carefully pre-

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[1] *Chem. Ztg.*, **35**, 1096 (1911).

[2] *Ber.*, **23**, 3023 (1890); **24**, 3341 (1891).

pared in this manner and kept in the dark, remains white for an indefinite length of time.

Preliminary Decomposition of Very Small Quantities of Silver Trinitride.—Preliminary experiments to ascertain the behavior up to the exploding point of the silver trinitride were made in a small ordinary melting point apparatus as follows:

To a 350° thermometer was attached at the lower end an ordinary melting-point tube in which was placed the trinitride. The tube was fastened about one cm. from the thermometer by platinum wires. The whole apparatus was then immersed in melted paraffin contained in a 50 cc. Jena glass round-bottom flask, supported in a sand bath. The operator was protected from possible explosions by a heavy glass screen. Several very small samples of silver trinitride were decomposed by the method just described, and observations were made upon the melting point, decomposition point, and explosion point. When treated in this manner the compound first begins to turn slightly violet at about 150°, the color increasing somewhat in intensity until a temperature somewhat above 250° is reached, when the compound melts down to a blackish looking liquid which begins to liberate gas or vapor at about 253.5°. This appearance of boiling continues as the temperature is raised until the substance finally shrinks to a brownish solid, which begins to turn white as the decomposition approaches the end, and finally is pure white when the decomposition is complete. Apparently the appearance of boiling mentioned above is not a true boiling condition, but simply the result produced by the escape of nitrogen during the decomposition. The temperature measurements obtained in 3 experiments were as follows:

	Expt. 1.	Expt. 2.	Expt. 3.	Average.
Melting point	252°	251°	251.5°	251.5°
First appearance of ebullition	254°	253°	253.5°	253.5°

In each of the above experiments the salt was entirely decomposed without explosion.

To ascertain the temperature at which explosion would take place, larger quantities of the silver trinitride were heated quite rapidly until a temperature of 280° was reached and then more slowly until they exploded.

	Expt. 1.	Expt. 2.	Expt. 3.	Average.
Explosion point	300.5°	301.0°	300.0°	300.5°

Curtius gives 250° as approximately the melting point for silver trinitride. No mention has been found in the literature concerning the point at which it begins to decompose when heated in this manner, but L. Wöhler[1] gives an exploding point about 300°. The determinations of

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[1] *Z. angew. Chem.*, 2, 2089 (1911).

the author were not made with an accurately calibrated thermometer, but seem to confirm the observations made by Curtius and by Wöhler.

Quantitative Decomposition of Silver Trinitride at Atmospheric Pressure.—For this work the method of decomposition was essentially the same as previously described. The trinitride was placed in a glass tube, about 20 cm. long and 4 mm. internal diameter, the sealed end of which we immersed in the paraffin bath. The upper end of the tube was sealed to a long glass tube communicating with a Schiff nitrometer.

The silver trinitride was gradually heated and the effect at different temperatures noted. The gas evolved was collected in the Schiff nitrometer and after thorough decomposition of the trinitride had taken place, measured and corrected to standard condition. The tube containing the silver was then cut off at some convenient point, was weighed, the silver then dissolved out with nitric acid and the tube dried and again weighed. The difference in weight thereby gives the weight of the silver residue. Several samples of silver trinitride from 0.02 to 0.4 g. in weight were decomposed in this manner with satisfactory quantitative results.

In these experiments it was found that nitrogen was given off but very slowly at the melting point (251°), or even slightly above the ebullition point (253.5°), although those temperatures were maintained for some time. The evolution of nitrogen increased quite rapidly as the temperature was raised. The silver obtained in the experiments was almost pure white, and when examined under the microscope, exhibited the appearance of a porous mass of metallic silver.

From these preliminary experiments it was found that for the surest and best quantitative decomposition of silver trinitride, a temperature of from 280 to 290° should be maintained with no greater increase of temperature than 0.5° per minute.

Preliminary Decomposition of Silver Trinitride in Torricellian Vacuum. Procedure.—It was now thought advisable to work under a Torricellian vacuum, and therefore, for the following experiments the apparatus shown in Fig. 1 was prepared. For the most part it is the same as has been used by other investigators in this laboratory on gas volumetric work. A few preliminary experiments were first made to ascertain the melting point, decomposition point, and exploding point, under these conditions. For this work the same type of heating apparatus was used as in the previous experiments, namely, a small flask of paraffin heated on a sand bath. The small bulb tube containing the trinitride was fused to the capillary tube just below N, the tube N in this case being removed. The bulb tube and connections were then evacuated by means of the mercury buret A, which was fitted with a two-way stopcock K, and connected to the calibrated mercury buret E.

Experimental Results.—The silver trinitride began to melt at 185°, had the appearance of boiling at 187.5°, at the same time decomposing with very slow evolution of nitrogen, and a slight condensation of a brownish substance on the cooler portion of the tube above the bulb. There seemed to be but little noticeable increase in nitrogen evolution until 260° was reached. The heating was increased very slowly from this point and the sample of 0.0836 g. was entirely decomposed before the explosion point was reached. The temperature measurements obtained in 3 experiments were as follows:

	Expt. 1.	Expt. 2.	Expt. 3.	Average.
Melting point............................	185.0°	186.0°	185.5°	185.5°
First appearance of ebullition...............	187.5°	187.5°	188.0°	187.7°

Several other samples of silver trinitride were decomposed in order to ascertain the ease of explosibility near the exploding point, and from this work as well as from the preceding experiments it was found that when heated in a Torricellian vacuum, silver trinitride is much more sensitive to sudden rise in temperature than when heated at atmospheric pressure, sometimes even exploding as low as 280°, especially when comparatively large amounts, 0.3 to 0.5 g., were used. Decomposition can, however, be effected in much less time *in vacuo* than at atmospheric pressure. Although the melting point and appearance of ebullition of silver trinitride is very much lowered by heating in a Torricellian vacuum, the exploding point remains practically the same.

Special Heating Apparatus.—At this point the necessity presented itself of securing a better means of obtaining easily regulated accurate temperatures, so the author conceived the idea that an electric furnace of the type shown in Fig. 1 would be about the best for the purpose. The furnace

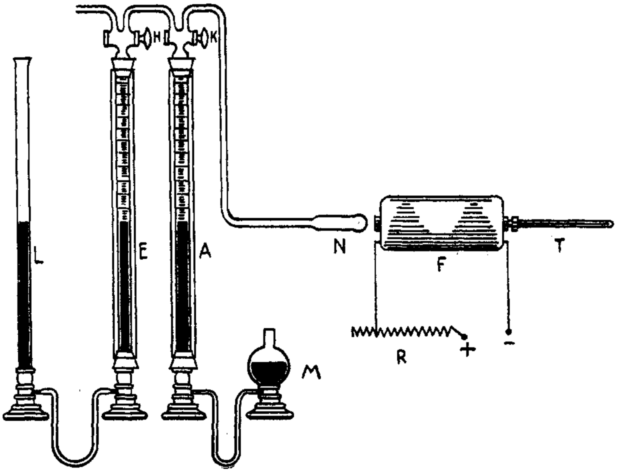

Fig. 1.

F was constructed as follows: an iron tube 32 cm. long and 1.5 cm. internal diameter was wrapped tightly with asbestos paper, then around this was wound somewhat closely many turns of German silver wire (0.017 inch in diameter); another wrapping of asbestos paper and then another coil of wire, etc., the furnace when complete having three coils. The whole was enclosed in an asbestos casing and had a diameter of 7.5 cm. Alternating current was used, the strength of current being regulated by means of a bank of lamps and sliding resistance, R. Each coil was capable of producing approximately 125° per ampere.

Quantitative Decomposition of Silver Trinitride in a Torricellian Vacuum. General Procedure.—The bulb tube N was cleaned, dried and heated in an air bath 105° for 15 minutes, cooled in a desiccator and weighed. The difference gave the weight of silver trinitride used. The bulb tube N was then fused to the capillary leading to buret A. The whole apparatus was then evacuated until a Torricellian vacuum was obtained. The bulb tube N containing the silver trinitride was now slipped into the iron tube of the electric furnace F, the current turned on, the temperature being indicated by the thermometer T and regulated by the sliding rheostat R. During the decomposition the gas evolved was collected in buret A and was then measured in the calibrated buret E. After complete decomposition had taken place, the tube N containing the silver was broken off and weighed. The silver was dissolved out and the tube dried and again weighed, the difference in weight giving the weight of the silver. This was checked by determining the silver as chloride.

	Expt. 1.	Expt. 2.
Weight of silver trinitride used	0 7638 g.	0.7782 g.
Loss in weight due to decomposition	0.2141 g.	0.2180 g.
Theoretical weight of nitrogen in the sample of AgN_3	0.2142 g.	0.2182 g.
Weight of residue after decomposition	0.5497 g.	0.5602 g.
Theoretical weight of silver in the sample of AgN_3	0.5496 g.	0.5600 g.
Volume of nitrogen corrected to standard conditions	171.6 cc.	174.2 cc.
Theoretical volume of nitrogen under standard conditions contained in sample of AgN_3 used	171.2 cc.	174.4 cc.
Weight of silver chloride	0.7305 g.	0.7440 g.
Weight of silver in the sample of AgCl	0.5498 g.	0.5599 g.
Total time of decomposition	310 min.	355 min.

During both of these experiments the temperature was increased fairly rapidly (about 15° per minute) from room temperature to 250°; from this point to 275°, 5° per minute, and finally 1° per minute from 275 to 285°. A temperature of 285 to 288° was then maintained throughout the remainder of the decomposition. After all evolution of nitrogen had ceased the temperature was gradually increased, then rapidly until about 400° was reached, thus insuring the complete expulsion of the nitrogen. The appearance of the silver after the decomposition was similar in every respect to that obtained in the previous experiments.

The nitrogen evolved in each case was analyzed for oxygen (as check against leakage) by means of phosphorus, but in the above experiments not the slightest indication of oxygen was detected.

Effect of Temperature and Duration of Heating upon the Rate of Decomposition of Silver Trinitride.—In order to ascertain if there was any possibility of an intermediate compound, such as Ag_3N, being formed during the process of decomposition, experiments were performed at various temperatures and in which the volume of gas evolved in each 5-minute interval was carefully noted.

In all of these experiments it was noticed that no definite cessation of gas evolution occurred at any time through the entire decomposition and that the rate of evolution remained practically uniform for any given temperature; but if the temperature was allowed to increase somewhat rapidly, even for a few degrees, the rate of decomposition increased very markedly for a few minutes and then gradually proceeded at a uniform rate.

To ascertain further the nature of the substance undergoing decomposition, several samples were decomposed until one-third and two-thirds, respectively, of the theoretical amount of nitrogen had been evolved. At these stages the substance was taken out and examined under the microscope and its explosive temperature measured. In all cases the microscope revealed glistening portions of metallic silver, showing that the decomposition had not been uniform throughout the whole mass. When heated, the exploding temperature was the same as for the original silver trinitride.

Decomposition of Certain Other Inorganic Trinitrides.

The experimental procedures with the following trinitrides were essentially the same as those used with the silver trinitride, except that in many cases the study was not carried out with as great detail.

Mercurous Trinitride.—When heated under the prevailing atmospheric pressure, the mercurous trinitride remained practically white until a temperature of 220° was reached, when it began to turn yellow and sublime somewhat on the colder portions of the tube directly above the substance. The color increased in intensity as the temperature was raised, becoming reddish, reddish brown, and finally almost black. No indications of a melting point were observed. The evolution of gas seemed to begin at about 215° and increased in rapidity until the exploding point was reached, which in most of the experiments was found to be about 270°. The best temperature for the safe decomposition of the trinitride was found to be about 250°. Mercurous trinitride decomposed with much less ease than silver trinitride and required much more skilful manipulation. As the decomposition proceeds globules of metallic mercury collect upon the cooler upper portion of the tube, and in the quantitative determinations which were made, a small weighed piece of gold foil was placed in the tube just beyond where the mercury collected, in order to retain any vapors of mercury that might be carried beyond.

From a number of experiments it was shown conclusively that mercurous trinitride can be decomposed quantitatively, without explosion, into its elements.

Mercuric Trinitride.—This substance was found to be very sensitive to concussion or friction, especially when prepared from mercuric nitrate and sodium or potassium trinitride, and should be handled with much care. The compound, when heated at atmospheric pressure in the manner previously described for other trinitrides, began to evolve gas at 212°, apparently to boil at 215°, and at the same time to evolve gas slowly, the changes in color and manner of sublimation were similar to that observed for mercurous trinitride. The evolution of nitrogen proceeded at a much faster rate and with greater ease than in the case of mercurous trinitride. The normal exploding temperature was found to be about 300°, but if great care was not exercised in the heating, the compound was found to explode at a much lower temperature. Several samples were decomposed quantitatively in the same manner as the mercurous trinitride; in fact, it proved to be the better of the two for decomposition work.

Lead Trinitride.—This salt was found to be extremely hard to decompose without exploding; out of nine attempts to decompose it quietly, only one proved successful and in this case only a small quantity (0.0537 g.) of the substance was used. The temperature at which this decomposition was accomplished was 245 to 250°. The normal exploding temperature seems to be about 360°, but in most cases it would explode much below that point if the temperature was not regulated carefully. The compound seems to decompose and explode before the melting point is reached.

Cupric Trinitride.—Of all the trinitrides studied in this investigation cupric trinitride proved to be the most difficult to decompose without exploding; in fact, the writer has not been able to decompose it to any appreciable extent, although numerous attempts have been made to do so.

Thallous Trinitride.—In the study of this compound it was found that the salt underwent no noticeable change until a temperature of about 330° was reached, when it melted down into an almost colorless liquid which soon began to sublime (340°) on the cooler portion of the tube. Nitrogen began to evolve slowly at 370° and increased quite rapidly as the temperature was increased, the compound exploding when a temperature of about 430° was attained.

Of the trinitrides studied in this series, thallous trinitride was decomposed more quickly and with greater ease without danger of exploding than any of the others, the only difficulty being its tendency to sublime. This was overcome by inserting a high temperature electric furnace immediately beyond the decomposition furnace F, Fig. 1. By use of this arrangement several samples of thallous trinitride were quantitatively decomposed, the thallium remaining in the tube as pure white metallic metal.

Barium Trinitride.—This compound showed no apparent change until a temperature of about 180° was reached, when a very slow evolution of nitrogen took place and continued to increase until the exploding point was reached, which seemed to be about 225° in most cases. It was found quite difficult to regulate the temperature so as to get a slow decomposition, the tendency being to decompose very rapidly, but with not enough violence, however, to break the tube. Out of 5 experiments the writer succeeded in decomposing slowly but one sample. In all cases where the sample was decomposed rapidly (that is, with a slight puff), the decomposition seemed to be complete, and the metallic barium was deposited on the walls of the tube in the form of a fine black powder, which, when exposed to the air or thrown on water, quickly took fire. Decomposition of quantities as large as 0.50 g. of barium trinitride was easily effected.

Ammonium Trinitride.—Only a few preliminary decompositions of this compound were attempted. When ammonium trinitride was subjected to heat in the same manner employed for the other trinitrides studied in this investigation, the products of decomposition were ammonia, nitrogen and hydrogen. Considerable difficulty was experienced in completely decomposing the salt on account of its tendency to sublime.

Potassium Trinitride and Sodium Trinitride.—Only preliminary determinations were made upon these compounds. Their manner of decomposition was very similar to that of barium trinitride, except that metallic potassium, and sodium, were deposited on the sides of the decomposition tube in the form of a mirror. The decomposition was not violent enough, however, when carried out in a Torricellian vacuum, to break the tube.

Summary.

The principal results obtained in the present investigation may be summarized as follows:

1. Silver trinitride, when carefully heated just below 300°, the normal exploding temperature of the compound, was completely decomposed in a satisfactory manner into pure metallic silver and nitrogen. It was found that for the surest and best decomposition of silver trinitride, a temperature of from 280 to 290° should be maintained with no greater increase than 0.5° per minute.

2. The rate of decomposition of silver trinitride was found to increase with an increase of temperature, and this decomposition took place more rapidly when quickly heated, but the tendency to explode was much greater.

3. When silver trinitride was decomposed in a Torricellian vacuum, the evolution of nitrogen was much more rapid than at atmospheric pressure. The melting point was considerably lowered, but the exploding temperature remained practically the same as when carried out under atmospheric pressure.

4. So far as can be ascertained, no definite intermediate compounds were formed during the decomposition of the silver trinitride.

5. It has been shown that mercurous, mercuric, barium and thallous trinitrides can also be satisfactorily and quantitatively decomposed into their elements, but lead, cupric, and ammonium trinitrides have not given very satisfactory results in this respect.

6. An ideal method has been satisfactorily devised whereby the atomic weight of nitrogen can very accurately be determined, and from this knowledge one can thereby easily determine the atomic weights of a number of the metallic elements which form trinitrides, by decomposing these trinitrides into their elements and weighing each directly.

In conclusion, the author wishes to express his gratitude to Professor A. W. Browne, who has suggested the present investigation and under whose direct supervision it has been carried out.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREEZING POINTS OF CONCENTRATED SOLUTIONS AND THE FREE ENERGY OF SOLUTION OF SALTS.

BY WORTH H. RODEBUSH.

Received May 22, 1918.

A great deal of work has been done upon the freezing-point depression of dilute salt solutions, but owing to the defects of the experimental methods used many of the results are in error. In the case of concentrated solutions and eutectic mixtures of ice and salt the data are even more meager and unreliable. Since the freezing-point-concentration curve of a salt solution affords a direct means of calculating the free energy of solution for the salt, it seemed desirable to determine this curve for a number of salts of various types. This has been done in this investigation for the commoner salts, which are readily soluble below 0°.

Experimental.

The most accurate method of measuring freezing-point depression has been worked out by L. H. Adams[1] and used by him in measuring the

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[1] L. H. Adams, THIS JOURNAL, 37, 481 (1915).