IX. *On the Union of Ammonia Nitrate with Ammonia. By* EDWARD DIVERS, *M.D. Communicated by Professor* ODLING, *M.B., F.R.S.*

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1. AMMONIA nitrate possesses the somewhat remarkable property of combining with large quantities of ammonia. The product is a liquid the composition of which varies with the temperature and pressure to which it is subjected. It appears from its properties to be a solution of ammonia nitrate in liquefied ammonia, analogous in every respect to an aqueous solution of a salt, its formation being a phenomenon precisely like that of the deliquescence of a salt in a moist atmosphere.

2. The liquid was prepared by bringing dry ammonia gas into contact with dry ammonia nitrate in a flask loosely closed by a vulcanized caoutchouc stopper (to diminish loss of ammonia by diffusion) and imbedded in ice. The tube conveying the ammonia passed through the stopper and reached nearly to the bottom of the flask.

Care was taken to ensure as much as possible the absence of moisture. The nitrate was dried either by leaving it for a month or more spread out in crushed crystals on the floor of an air-tight glass chamber, in which were placed dishes of oil of vitriol, or by exposing it for some hours in an oven to a temperature only a little below its melting-point*. The nitrate was put into the dry and warm flask with as little exposure as possible, by scooping it up rapidly with the mouth of the flask direct from the vessel in which it had been dried. The flask was then at once closed and kept so until all arrangements were complete for passing the ammonia into it. The ammonia was dried by sending it through a glass tube more than 50 centimetres long, closely packed with very small pieces of stick potash; but before entering this tube it was deprived of most of its moisture by being made to pass through a long coiled tube surrounded with ice and thus cooled.

3. The condensation of the ammonia by the nitrate takes place slowly at ordinary temperatures, and in the cooled flask is complete until the point of saturation with ammonia is approached. The nitrate soon shows signs of deliquescence in the ammonia, and, after awhile, entirely liquefies. The resulting liquid still, however, possesses the power of condensing ammonia, and that to a considerable extent; while, on the other hand, the liquid saturated with ammonia can dissolve an additional quantity of ammonia nitrate. Raising the temperature of the liquid, loss of ammonia being

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* As the latter proved a less certain method of obtaining the nitrate quite dry, in consequence apparently of slight decomposition of the nitrate, the former only was employed in preparing the specimens of the liquid intended for the determination of its physical properties.

prevented, increases its capability of dissolving more nitrate, and lessens that of condensing more ammonia. On cooling the liquid, saturated or nearly so with nitrate, some of the salt crystallizes out in long prisms, exactly like those that form in an aqueous solution; on restoring the temperature these crystals redissolve. When the liquid is warmed, it gives off ammonia gas with the phenomenon of ebullition, not that of effervescence. Like many aqueous solutions, the liquid can be heated a little above its boiling-point without boiling, and be cooled below its crystallizing point without crystallizing, until it is disturbed, when ebullition or crystallization, as the case may be, takes place with suddenness. On boiling away the ammonia, or expelling it at a temperature below that of ebullition, the nitrate crystallizes out, just as it would do in similar circumstances from its aqueous solution. When the liquid is exposed to the air it instantly becomes crusted over with a film of nitrate, which is coherent, transparent, and apparently not crystalline. In consequence of this the liquid poured out on to a flat surface, sometimes even in the act of flowing from the mouth of the bottle, takes the appearance, though not the consistence, of jelly. On touching this apparent jelly, unchanged liquid breaks through the crust; and by stirring the mass about in a dry atmosphere, nothing but solid ammonia nitrate at length remains. When the crust is not broken, it preserves the enclosed liquid for a long time from further evaporation in dry weather.

The liquid is colourless, and as mobile as any aqueous saline solution. It smells very powerfully of ammonia, unless it be allowed to crust over, when this smell is almost wanting. It has not a slimy feel between the fingers like an alkali lye, and seems, indeed, to have no caustic power. It boils when poured on the skin, and gives rise to a slight feeling of crepitation, but it produces only a feeble sensation of cold.

4. The quantity of ammonia that can be condensed by the nitrate varies with the pressure and temperature, and appears to be quite independent of the atomic relations of the two substances. At the pressure of the atmosphere and at a temperature of 0°, ammonia nitrate can condense almost exactly half its weight of ammonia. Its condensing-power, therefore, exceeds that of water at the same temperature. The ratio of two parts nitrate to one of ammonia is about that of $3NO_3H \,.\, NH_3 : 7NH_3$; but there is nothing to support the view that the liquid is a definite molecular combination.

To determine the limit just stated of the condensing-power of the nitrate upon ammonia gas, at 0° and the atmospheric pressure, the closed flask containing the nitrate was weighed, and from the weight found was deducted that of the empty flask, its stopper, and an iron wire that served both to suspend the flask to the balance and also afterwards to bind down the stopper. The flask generally employed was one adapted for taking the specific gravity of the liquid, and which shall be more particularly described in connexion with that operation. The quantity of nitrate employed weighed from 35 to 45 grains. When the ammonia had been passed into the flask, surrounded with ice, for some time after absorption had apparently ceased, the delivery-tube was withdrawn, the flask at once closed, and the stopper wired down. The flask was then removed from the ice, left to regain the atmospheric temperature, and again weighed. The delivery-tube on removal from the flask was washed, the washings were evaporated, and the nitrate left as residue weighed. By deducting the weight of this nitrate from that of the whole quantity put into the flask, the weight of this salt in the liquid was ascertained; and by deducting this from that of the liquid, the weight of the ammonia condensed was obtained.

The smallest quantity of ammonia sufficient to liquefy the nitrate at 0° is a little more than one third of its weight. This point was determined by boiling away some ammonia from the liquid containing more than sufficient of it, until on cooling to 0° the liquid just began to crystallize. This method, for several reasons, is not a very accurate one for the purpose, one reason being that the liquid is apt to exhibit to some extent, as already stated, the phenomenon of supersaturation; but it was employed for want of a better, that would not have entailed trouble disproportionate to the importance of an accurate determination of this point at present.

At 23°, the temperature at about which the nitrate and ammonia cease to unite at the atmospheric pressure, the ratio of the quantities that form the liquid is that of 100 nitrate to 26 ammonia. This ratio was determined by first condensing, under the guidance of some previous experiments, about 27, parts of ammonia upon 100 of nitrate in the flask, dissolving up the whole of the nitrate by warming and agitating the contents of the closed flask, and then loosening the stopper and cautiously allowing the ammonia to boil off until on cooling the liquid to 20° the nitrate began to crystallize out. The stopper was then closely inserted again, and the temperature raised very slowly by means of a water-bath until the nitrate, by continued agitation, had all redissolved, save a very minute crystal. The temperature required to effect this resolution exceeded 28°. On now allowing the flask to cool very slowly in the (glass) water-bath and watching the crystal, it was not observed to show any increase in size until the temperature had fallen to 22°·5, when its enlargement became distinct. The liquid was therefore regarded as saturated with nitrate at 23°. It was also about saturated with ammonia, because beyond this temperature ammonia ceases to be condensed by the nitrate at the atmospheric pressure, and to this the liquid had been exposed. By now ascertaining the weight of the liquid and deducting that of the nitrate, the above ratio was obtained.

5. In the conjoint liquefaction of ammonia nitrate and ammonia heat must be consumed by the nitrate in passing from the solid to the liquid state, and be generated by the ammonia in passing from the gaseous to the liquid state. The heat produced by the latter change proves to be in excess of that consumed by the former, even when, by keeping the nitrate in excess, the greatest relative liquefaction of this salt is ensured; that is to say, the formation of the liquid is always attended with the evolution of heat. On the other hand, as already described, the destruction of the compound is attended with the production of cold.

As was stated in the previous section, the temperature above which ammonia nitrate and ammonia cease to unite is about 23°–24°; for on bringing these bodies in contact at a temperature *below* 23°, this soon rises to that of 23°–24° (the temperature evidently varying with the atmospheric pressure) and remains at this point, even (after some liquefaction has taken place) when the ammonia, before it comes in contact with the nitrate, is heated several degrees *above* 23°, the result in this case being, without doubt, due to the destruction that then takes place of the liquid already formed.

The boiling-point of the liquid, when saturated with nitrate at 23°, was found to be about 26°; but as the liquid boils irregularly, it is very probable that the true boiling-point lies a few degrees below this.

6. For the purpose of taking the specific gravities of the products obtained by using different proportions of ammonia and nitrate, a flask was employed having a long graduated neck. Different quantities of nitrate were weighed in it, and then into each quantity ammonia gas was passed until the resulting liquid filled it at 15°·5 to some point in the neck. The body of the flask was globular, had stout walls, and contained nearly 46 cubic centimetres. The neck consisted of a piece of barometer-tube, surmounted by a larger tube, into which it abruptly expanded. This part of the neck served as a funnel, and also to receive any of the liquid carried by the bubbles of ammonia above the top of the narrow tube. It was made without everted lip, so as to facilitate the scooping up of the nitrate by it. The shoulder it formed with the narrow part of the neck served to retain the wire used to bind down the caoutchouc stopper. The narrow, graduated part of the neck was about 7 centimetres long, and had an internal diameter of about 6½ millimetres. The weight of water at 15°·5 held by the flask to the level of every twentieth graduation, of which there were sixty-five, was experimentally determined; intermediate quantities were calculated. The delivery-tube for the ammonia was a slender one, in order that it might leave as much room as possible in the neck for the rise of bubbles through the liquid; but even with this arrangement the liquid sometimes rose into the funnel, and did not always satisfactorily drain down again.

The following specific gravities were taken:—

No.	Ammonia nitrate.	Ammonia.	Specific gravity.
1. . . .	1000 parts.	495·5 parts.	1072·5
2. . . .	1000 „	392·5 „	1119·95
3. . . .	1000 „	385 „	1126·05
4. . . .	1000 „	334 „	1155·9
5. . . .	1000 „	316·5 „	1167·05
6. . . .	1000 „	281·5 „	1191·65
7. . . .	1000 „	272 „	1199

(The liquid No. 7 crystallized when cooled to the standard temperature, so that its specific gravity had to be taken at a higher one, and from this its specific gravity at

15°·5 calculated by means of its approximate coefficient of dilatation, which was determined by other observations.)

By taking the numbers expressing the specific gravity and composition of Nos. 1 & 6, it is easy to compute the specific gravity of the excess of the ammonia in No. 1 over that in No. 6, on the assumption that the latter liquid undergoes no change in density by uniting with more ammonia. On making the further assumption that all the ammonia condensed by the nitrate has the same density, the specific gravity of the nitrate in the liquid can also be calculated; or this can be found directly for the excess of the nitrate in No. 6 over that in No. 1 in union with the same weight of ammonia, in the same way as that for the ammonia was calculated. On then calculating from the weights of the two substances, and the specific gravities thus found for them, the specific gravities of the liquids the composition of which is given in the preceding Table, the assumption that the densities of the two substances are constant is found to be correct, in so far, that is, as the results are concerned. The calculated specific gravity of the ammonia is 671, and that of the nitrate 1524·5. The specific gravities of the liquids calculated from these numbers are placed in the following Table by the side of those found by experiment, and their almost entire identity within the limits of experimental error thus rendered apparent:—

No.	Calculated.	Found.
1.	1072·5	1072·5
2.	1122·0	1119·95
3.	1126·3	1126·05
4.	1156·1	1155·9
5.	1167·35	1167·05
6.	1191·45	1191·65
7.	1198·55	1199·0

Except in the case of No. 2 the differences between the two series of numbers are quite within the limits of experimental error, and in that case some unobserved error no doubt must have been made in the determination.

The calculated specific gravity of the ammonia in these liquids (671) is greater than that found for ammonia liquefied by pressure by Andréeff* (615·5 at 15°·5) or by Jolly† (623·4 at 0°). Griffin‡ has calculated the specific gravity of ammonia liquefied by water to be constantly 708, on the usual assumption that the density of the water is constant, a number not far from that found by Faraday§ (731) for ammonia liquefied by pressure. The calculated specific gravity of the nitrate in the liquid (1524·5) is much less than the number (1740) found for the solid nitrate by Karsten‖, that by Kopp¶ (1707), or that by Playfair and Joule** (1635); it is also much less than the

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* Ann. Chim. Phys. [3] lvi. p. 317.

† Ann. Ch. Pharm. cxvii. p. 181.

‡ Mem. Chem. Soc. iii. p. 155.

§ Phil. Trans. (1845) p. 169.

‖ Ber. Abhandl. (1840) p. 95.

¶ Ann. Ch. Pharm. xxxvi. (1840) p. 1.

** Mem. Chem. Soc. ii. p. 436.

calculated specific gravity of the nitrate in dilute aqueous solution, namely 1758, according to Playfair and Joule. But the observations of Thomsen* show that the specific gravity of the nitrate appears to vary from about the number obtained by Playfair and Joule to that of 1565·5 at 18°, in a solution of 8 of nitrate in 9 of water; and I have myself found it to have in a solution of 12 nitrate in 7 water an apparent specific gravity of 1572·5 at 15°·5, a number not greatly exceeding that expressing its apparent density when liquefied by ammonia. The ammonia and the nitrate in the liquid have therefore each a less apparent density than they have when dissolved in water, and the nitrate a much less apparent density than its actual density in the solid state.

7. The flask used for determining the specific gravity served also for some rough determinations of the expansivity by heat of the liquids of different composition. By observing the height of the liquid at 0°, and again at 15°·5, the expansion between these temperatures was ascertained, and from this the expansion between 0° and 100° calculated, on the assumption that the expansion proceeds uniformly. The results obtained were the following:—

No.	Ammonia nitrate.	Ammonia.	Expansion from 0° to 100°.
1.	1000	495·5	about $\frac{1}{16}$
2.	1000	392·5	" $\frac{1}{17-}$
3.	1000	385	" $\frac{1}{17+}$
4.	1000	334	" $\frac{1}{17+}$
5.	1000	316·5	" $\frac{1}{18-}$

They are sufficient to prove that the expansivity of the liquid increases with the ratio of the ammonia to the nitrate; they also show that the expansivity of ammonia liquefied in this way is similar to that of other liquids existing as such under the pressure of the atmosphere, and far less than that of ammonia and other substances kept in the liquid state only by great pressure. Thus, from the experiments of Andréeff†, it appears that ammonia liquefied by pressure expands nearly $\frac{1}{22}$ of its volume when its temperature is raised from 0° to only 20°.

8. The volume of a mixture of the liquid with water is much less than the sum of the volumes of the liquid and the water used; and yet the admixture is attended with a considerable absorption of heat. The same remarkable phenomenon is manifested when a concentrated aqueous solution of the nitrate is mixed with water, and, indeed, by concentrated aqueous solutions of other salts, though, I believe, not by any of them to the extent that it is by that of the nitrate in either water or liquefied ammonia. Person‡ calls the heat that thus disappears the *latent heat of dilution.*

When the liquid of specific gravity of 1191·65 (No. 6 in the preceding Tables), and composed of 1000 nitrate to 281·5 ammonia, was mixed with five times as much water as the weight of the nitrate in it, the admixture was attended with a fall of 4° C. in the liquids both at first at the temperature of the laboratory. In effecting the

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* Pogg. Ann. cxlii. p. 337.

† Ann. Chim. Phys. [3] lvi. p. 317.

‡ Ann. Chim. Phys. [3] xxxiii. p. 448.

admixture, the closed flask containing the liquid was inverted, with its mouth below the surface of the required quantity of water, and maintained there by a wooden holder; the wire retaining the stopper was then cut, and the latter removed by means of a pair of tongs. The liquid rapidly descended into the water and was replaced by the latter, which in its turn was replaced by air, by bringing the mouth of the flask just above the surface of the liquids. These were then at once briskly stirred round with a thermometer, and the altered temperature noted, the entire operation of mixing having occupied but a very short time. A specific-gravity bottle was immediately afterwards filled with the mixture, so that no appreciable loss of ammonia could have been sustained, the more so that the experiments were made in winter. Lastly, its specific gravity was taken at the standard temperature and found to be 1043·8. By assuming that the water undergoes no change in density, the specific gravity of the liquid after its admixture with the water can be calculated, and proves to be 1258·6 instead of 1191·6, its original specific gravity.

When a solution of 12 parts of nitrate in 7 of water, which is an almost saturated one at 15°·5, is mixed with 5 times 12 or 60 parts of water, there is also a fall in temperature of 4°, accompanied by condensation*: for before admixture the specific gravity of the primary solution is 1298·7, while afterwards its specific gravity, calculated from that of the mixture, 1064·4, is 1336; whence it will be seen that the contraction in volume, though very considerable, is not so great as that experienced by the ammonia solution of the nitrate, as might indeed be anticipated from the fact that the calculated densities of the nitrate and the liquefied ammonia are both less than their densities in aqueous solution.

When the liquid (No. 1 in the preceding Tables) containing the least proportion of nitrate, namely two thirds of its weight, was mixed with water in the proportion (for the sake of comparison) of five parts to one of the nitrate, the temperature was found to fall only about $\frac{1}{4}$°. The admixture was effected as before, except that on removing the stopper the liquid was in this case violently expelled from the flask into the water by some ammonia becoming gaseous, and that then the water rose into the flask by absorbing this gas. The specific gravity of the mixture was found to be 1026·4, and from this was calculated that of the liquid after its admixture with water. Instead of its original specific gravity, which was 1072·5, it had in the mixture that of 1125·8. Compounds of the nitrate with ammonia in other proportions were also mixed with water, and results obtained confirming those just detailed. The proportion of five parts water to one of the nitrate was chosen for the comparative experiments in order to have the mixture dilute, and therefore less liable to lose ammonia by diffusion ; with less water a greater depression of temperature would no doubt have been observed, but the investigation was not further pursued in this direction.

The small extent of the fall in temperature when the liquid containing the least

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* Gay-Lussac first observed the fall in temperature with contraction in volume that occurs when a concentrated solution of ammonia nitrate is diluted with water (Ann. Chim. Phys. i. p. 214).

proportion of nitrate is mixed with water, is to be attributed principally to the fact of the nitrate being in more dilute solution than in the other case described; for it is found on diluting a concentrated aqueous solution that the cold is produced in the earlier stages of the dilution. It is perhaps also to be attributed, to a slight extent, to the presence of more ammonia than in the other cases; since it is possible that ammonia in the liquefied condition may generate a little heat when mixed with water, and this must mask the cold produced by the nitrate to a corresponding extent.

The accompaniment of contraction of volume by absorption of heat, here illustrated, has received several explanations. GAY-LUSSAC, in accounting for it, considered that the specific heat of the mixture must be greater than the mean of the specific heats of the saline solution and the water; but THOMSEN'S[*] researches have shown that the specific heat of a mixture of an aqueous solution and water is *less* than the mean of the specific heats of the solution and water. THOMSEN has also pointed out that where (as in the case of the salts of the fixed alkalies) the molecular volume is greater than the sum of those of its constituents, the molecular heat of the compound is greater, and that, on the other hand, where (as in the case of ammonia salts) the molecular volume is less, the molecular heat is also less; so that it appears that volume and specific heat lessen and increase together.

Another explanation is one that has been offered by BUSSY and BUIGUET[†], whose attention was drawn to this subject by their observation of the simultaneous contraction in volume and absorption of heat that occurs when liquid hydrocyanic acid and water are mixed together, and who have established that no apparent relation exists in these cases between changes in volume and changes in temperature. They ascribe the production of cold to the diffusion of the one liquid through the other, by which, according to their notions, each occupies a greater volume than it did before. But although after admixture each liquid does extend through a greater space, it does not do so by undergoing an increase in volume, but by being displaced by the other liquid, the space occupied by the mixture being filled up by the two liquids conjointly—assuming, that is (as is necessary in applying the above explanation), that the two liquids preserve their individuality during admixture. Now, unless diffusion involves expansion, it is hardly evident how it can afford any solution of the difficulty.

F. MOHR[‡] has suggested that the heat which disappears is the excess of that used up in giving to the mixture the property of remaining liquid at a lower temperature than water itself can, over that evolved in giving it the property of remaining liquid at a higher temperature than the water. This is apparently to assume that the latent heat of water is variable and inversely related to the temperature of freezing, just as the latent heat of steam is variable and inversely related to the temperature at which it is formed; and the assumption seems probable enough.

The anomaly that presents itself, when the density of the water is considered to

[*] POGG. Ann. cxlii. p. 337; Chem. Soc. Journ. [2] ix. p. 468.

[†] Ann. Chim. Phys. [4] iv. p. 5.

[‡] Deut. Chem. Ges. Ber. iv. p. 314.

remain constant during the dissolution of a salt in it, of the nitrate having in concentrated solutions a greater, and in dilute solutions a less volume than it has in the solid state, disappears by supposing that while the salt always undergoes during solution the contraction in volume so evident when the proportion of water is large, the water undergoes slight dilatation: for then it follows that when the salt is dissolved in only a small quantity of water, the former will experience a less contraction and the water a greater expansion, and that thus there may be a total increase in volume; while when the salt is dissolved in a large quantity of water, the contraction of the salt will be in marked excess of the expansion of the water, and therefore will become evident in the increase in total volume. Dilute solutions of sodium carbonate and of some sulphates, having a less volume than the total water they contain, appear to afford an argument against the above supposition; but in these solutions the salts dissolved are not the anhydrous ones, but those with water of crystallization.

By dissolving ammonia nitrate in concentrated ammonia-water, the latter is affected in the same way as it would be by dilution with water, so far, that is, as the tension of the ammonia diffusing from its surface is concerned.

9. The chemical behaviour of the liquid, like its physical properties, tends strongly to show that it is simply a solution of ammonia nitrate in liquefied ammonia. As a solvent, it appears, from the brief abstract as yet published of Mr. GORE'S experiments[*], to resemble ammonia liquefied by pressure. But the ammonia nitrate modifies the solvent action of the ammonia in the same way that it does that of ammonia in aqueous solution. Its chemical properties are interesting, but in most instances such as might be expected in a mixture of ammonia nitrate and ammonia *in the absence of water*. The general effect of the liquid upon salts appears to be to convert them into ammoniated nitrates and ammonium salts of the stylous radicals.

As, however, a quantitative examination of the products would be attended with considerable difficulties from the nature of the liquid and the decomposition of the products by water, only a qualitative one has been attempted.

Bromine acts very energetically on the liquid, instantly dissolving in it without colour and liberating nitrogen. Ammonia hydrobromide is formed, and much of it deposited. No bromate is produced.

Chlorine has not been tried.

Iodine dissolves slowly, but to a considerable extent, in the liquid, with evolution of heat. No gas is generated. A very little of the iodine dissolves without imparting any colour, but the after portions colour it until it becomes of a rich, deep brown-red, and almost opaque. Very early during the dissolution of the iodine a crystalline deposit, apparently white, begins to form, and this continues to be produced until it renders the whole nearly solid. No diniodamine is formed. The iodine seems, therefore, to dissolve in the liquid either simply or in the form of MILLON'S compound—$N_2H_6I_2$[*]. Treated with water it yields nitrate and a little hydriodide in solution, and

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[*] Proc. Roy. Soc. xx. p. 441.

[†] Ann. Chim. Phys. lxix. p. 78.

a deposit of iodine containing some iodamine. Immediately the magma is exposed to the air, it takes the colour and metallic lustre of iodine (like MILLON'S compound), evidently from the escape of ammonia and deposition of iodine. Heated in a water-bath ammonia escapes, and in a little while iodine vapours along with it. The residual mass, apparently a mixture of ammoniacal salts and free iodine, gives up quantities of the latter to carbon bisulphide, and, by the application of a somewhat higher temperature, continues to give it off in vapour for some time. It then consists of ammonia nitrate and hydriodide, the latter in rather considerable quantity. As no iodate is formed, nitrogen must escape during the exposure of the mass to heat, in accordance with MILLON'S observations upon iodine and ammonia.

Phosphorus is very slowly stained throughout its mass of a brown colour, and a minute quantity of brown flocculent matter forms upon its surface, which is apparently unaffected by hydrochloric acid. After neutralization, the liquid smells of phosphoretted hydrogen, but no appreciable quantity of phosphorus is dissolved in it. (According to COMMAILLE [*], alcoholic ammonia gradually turns phosphorus brown, ammonia phosphite and hypophosphite being at the same time formed.)

Potassium, *sodium*, *zinc*, and *cadmium* dissolve without the evolution of gas, and convert the nitrate into nitrite. The alkali metals act with much the same energy that they do upon water, melting and rolling about on the surface of the liquid till dissolved, the potassium always inflaming: the nature of their action is best ascertained by using dilute amalgams of them. The dissolution of the zinc is soon accompanied by the deposition of a bulky crystalline matter, apparently an ammoniated zinc nitrate. Cadmium dissolves only slowly. (Free ammonia so greatly intensifies the action of zinc and cadmium upon an aqueous solution of a nitrate, that STAHLSCHMIDT[†] prepares nitrites in this way.)

Magnesium is slowly dissolved with the evolution of hydrogen and the formation of nitrite. The surface of the metal becomes covered with a black deposit, which immediately turns white on contact with the air. This black matter is probably the suboxide of magnesium, which was observed by BEETZ[‡] to be formed when a solution of salt was electrolyzed with magnesium electrodes.

Hydrogen, *nitrogen*, *oxygen*, *carbon*, *sulphur*, *iron*, *aluminium*, *nickel*, *tin*, *lead*, *bismuth*, *copper*, *mercury*, *silver*, and *platinum* are unaffected. Traces of lead and bismuth are found in the liquid, but probably these are dissolved oxides. Copper in the presence of air dissolves as it does in aqueous ammonia, but less readily.

Ammonia hydrochloride slowly dissolves to a moderate extent. Most chlorides are either dissolved or converted into ammonia hydrochloride and an insoluble or nearly insoluble ammoniated compound.

Potassium chloride is sparingly soluble.

Sodium chloride cakes together, and only dissolves to a slight extent.

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[*] J. Pharm. Chem. [4] xiv. p. 184.

[†] POGG. Ann. cxxviii. p. 466; Suppl. Watts's Dict. Chem.

[‡] POGG. Ann. cxxvii. p. 45.

Silver chloride and *barium chloride*[*] slowly dissolve to a moderate extent.

Lead chloride dissolves freely. The solution may be mixed with several times its volume of water before precipitation begins to take place.

Calcium chloride and *cupric chloride* also dissolve freely, but the dissolution is at length attended with deposition of crystalline matter. The cupric solution is of the usual deep blue colour.

Magnesium chloride, *zinc chloride*, and *cuprous chloride* dissolve to a moderate extent, any excess that may be present being converted into white, bulky, crystalline deposits, soluble in water. The cuprous deposit and solution rapidly turn blue on exposure to the air.

Mercuric chloride dissolves sparingly. Water does not throw down any thing when added to the solution, white precipitate being soluble in ammonia nitrate (BRETT).

Mercurous chloride is decomposed into metallic mercury (a grey precipitate assuming the form of globules when washed and dried) and ammoniated mercuric salt, which dissolves.

Nickel chloride (bright yellow) becomes a bulky lilac-coloured mass, with slight evolution of heat. The liquid remains colourless, and takes up no nickel compound, but much (ammonium) chloride. The lilac deposit is soluble in water, with a lilac-blue colour.

Cobalt chloride is very slowly converted into a bulky red-brown mass, soluble in water with a brown colour. The liquid remains colourless, and takes up no cobalt compound, but some (ammonium) chloride.

Manganese chloride becomes a bulky white mass. The liquid dissolves only a very little manganese compound, but much (ammonium) chloride. The white deposit dissolves in water, yielding a solution only slowly precipitated by ammonia hydrosulphide.

Ferrous chloride (white scales or crystals) becomes a bulky white or nearly white mass. The liquid dissolves only a minute quantity of ferrous compound, and not much chloride. The white deposit dissolves in water, but very rapidly oxidizes and deposits ferric hydrate.

Ferric chloride is converted, with energetic action, into a bulky whitish chocolate-coloured mass. The liquid remains colourless, and takes up only a trace of ferric compound, but plenty of chloride. The deposit is converted into ferric hydrate by water.

Chromic chloride (violet) is only very slowly acted upon, being converted into a dull whitish-pink mass, which imparts to the liquid a cobalt-nitrate-red colour. The deposit is insoluble in water. The liquid may be mixed with water and acidified without experiencing any change of colour; but when heated with hydrochloric acid it changes to a pale chrome-alum colour, and then yields chromic hydrate with ammonia. The liquid may also be made to yield chromic hydrate by nearly neutralizing it with dilute hydrochloric acid and then boiling it.

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[*] This and all substances tried were used in the anhydrous condition, except where otherwise stated.

Aluminium chloride is gradually converted into a bulky mass, insoluble in water. The liquid takes up a trace of aluminium compound and much chloride.

Phosphorus chloride reacts violently, yielding a white bulky deposit. The liquid takes up much chloride, but only a very little phosphorus compound. The deposit dissolves in water, and gives the reactions of a phosphite.

Phosphoric chloride acts at the surface of the lumps very energetically, a result no doubt of its having absorbed moisture; otherwise it is only very slowly converted into a bulky white deposit, soluble in water. The liquid dissolves out much chloride, but only a little phosphorus compound.

Arsenious chloride is rather energetically converted into a bulky white deposit. The liquid holds much chloride in solution, but no arsenic compound. The deposit is soluble in water.

Antimonious chloride is slowly converted into a heavy white substance, insoluble in water, soluble in warm hydrochloric acid. The liquid takes up much chloride, but no antimony compound.

Antimonic chloride is converted into a bulky precipitate, which only very slowly deposits. The liquid takes up much chloride, but no antimony compound.

Bismuth chloride becomes a bulky mass. The liquid dissolves out no bismuth compound, but much chloride.

Stannic chloride acts with only slight energy, and yields a flocculent precipitate, which, when the chloride has been gradually and well mixed with the liquid, is perfectly soluble in water, the solution becoming clouded when heated. The liquid holds chloride in solution and a little tin compound, and when mixed with water becomes milky, either at once or upon heating.

Platinous chloride is first converted into MAGNUS's green salt, and then rapidly takes up more ammonia and passes into tetrammonio-platinous chloride, much of which dissolves in the liquid. There is sometimes also formed a perfectly white bulky precipitate, insoluble, or nearly so, in water, which is probably a modification of diammonio-platinous chloride.

Platinic chloride (either in the ordinary dry state or after it has been heated till both the water and hydrochloric acid combined with it have been expelled) is scarcely acted upon. Its surface becomes paler, and a trace of it dissolves in the liquid.

Auric chloride (in commercial crystals) is converted into a bulky, orange-coloured, crystalline matter, and at once renders the liquid bright yellow, although not much of it dissolves. The liquid gives a small precipitate of auric hydrate when mixed with water. The orange-coloured deposit is also converted into the hydrate by water.

Sulphur chloride (yellow) reacts very energetically, and gives brown fumes which coat the exposed part of the tube with a brown deposit ($N_2 S$?). When the liquid is kept cool during the admixture of the chloride it assumes a handsome violet colour, which soon passes to a yellow one, and then entirely fades away, with a deposition of sulphur; the liquid then appears to contain one or more of the thionic acids. When the mixture is made, a variegated mass is deposited, consisting apparently of plastic sulphur and a white salt of a thionic acid.

Carbon tetrachloride is insoluble.

Ammonia hydrobromide, *potassium bromide*, and *potassium iodide* behave like the corresponding chlorides.

Lead iodide dissolves readily. Like that of the chloride, the solution may be mixed with a considerable quantity of water before precipitation takes place. The precipitate that falls is white.

Mercuric iodide (red or yellow form) is turned perfectly white, and then rapidly dissolves to a considerable extent. The addition of water at once causes a curdy white precipitate to fall, which contains almost all the mercury and iodine. This precipitate becomes pale yellow when washed, and then suddenly scarlet-red. The effect of the liquid upon the iodide is quite distinct from that of ammonia and ammonia nitrate dissolved in water.

Fluorspar is insoluble.

Potassium cyanide is nearly insoluble.

Potassium ferrocyanide is very nearly insoluble, but swells up to a bulky mass.

Potassium ferricyanide at once imparts a strong yellow colour to the liquid, and is gradually converted into a pale yellow matter. Both the deposit and the liquid give the reactions of a ferricyanide.

Sodium sulphide reacts with some energy and forms a bulky deposit (sodium nitrate). The liquid becomes charged with ammonia hydrosulphide and fumes strongly in the air.

Zinc sulphide, *cadmium sulphide*, *lead sulphide* (native), *mercuric sulphide* (vermilion), and *antimony sulphide* (native) are insoluble and unchanged. (The least trace of zinc oxide in the zinc sulphide is dissolved out by the liquid.)

Ferrous sulphide and *manganous sulphide* (prepared by twice strongly igniting the sulphates with sulphur and cooling them in hydrogen) colour the liquid pale yellow. The manganous sulphide is partly converted into a bulky substance soluble in water. The liquid gives a slight precipitate of sulphur when mixed with water (sulphur itself is insoluble in the liquid); it also yields a slight brownish-black precipitate with lead acetate and acetic acid. On the other hand, it gives, in the case of ferrous sulphide, a slight black precipitate with ammonia hydrosulphide, and, in the case of manganous sulphide, a slight reaction with nitric acid and lead dioxide. (I am not confident that the process employed in preparing these sulphides yields them quite free from oxygen.)

Litharge is soluble. The solution gives a copious white precipitate with water. (Litharge is as efficient as lime or baryta in liberating ammonia from its salts.)

Quick lime hisses as it comes in contact with the liquid, causes an effervescence of ammonia, and dissolves, with the production of a viscid deposit (ammoniated calcium nitrate?).

Magnesia is for the most part converted into a gelatinous matter, but a little of it dissolves. Its action probably resembles that of lime.

Zinc oxide, *cadmium oxide*, and *cupric oxide* dissolve.

Mercuric oxide dissolves. The solution may be largely diluted with water without yielding a precipitate; and hydrochloric acid may be added to it without causing one until the liquid becomes acid, when a white one falls. Nitric and sulphuric acids give no precipitates. Sodium hydrate gives a yellowish precipitate, and potassium iodide a pale yellow one, turned scarlet-red by acids.

Cobalt oxide is slightly soluble, and colours the liquid a faint red-pink. The liquid gives a slight precipitate with ammonia hydrosulphide, which increases on standing.

Ferric oxide. A minute quantity of it dissolves and is thrown down by water as ferric hydrate.

Chromium trioxide reacts rather violently, and is converted into a yellow substance (ammonia chromamate?), quite insoluble in the liquid, but freely soluble in water.

Molybdenum trioxide is converted into a bulky white substance (ammonia molybdamate?), which is insoluble in the liquid, but soluble in water.

Arsenic trioxide is converted into a coherent mass, insoluble in the liquid, soluble in water.

Phosphorus pentoxide reacts rather energetically at the surface of the mass, in consequence no doubt of absorbed water (see *phosphoric chloride*). The rest of the oxide is very slowly acted upon, and undergoes no change in appearance. Much of it dissolves, probably as phosphamate (phosphates are almost or quite insoluble). The changed oxide dissolves quietly in water, and gives the reaction of a phosphate.

Boron oxide is very slightly soluble. The undissolved portions are unchanged in appearance, but the (vitreous) fragments of it become opalescent in water.

Carbon dioxide forms a solid substance, some of which dissolves in the liquid, and which is no doubt ammonia carbamate.

Silica, *alumina*, *tungsten trioxide*, *chromium sesquioxide*, *tin dioxide*, *manganese dioxide*, and *lead dioxide* are unaffected.

Carbon bisulphide is insoluble, but gradually combines with the ammonia.

Potassium hydrate causes an effervescence of ammonia, and rapidly dissolves. Its dissolution is followed by the deposition of most of the potassium as an insoluble compound, which is probably the nitrate.

Sodium hydrate is only slowly acted upon. A little of it dissolves, a crystalline matter (sodium nitrate) is deposited, and the liquid becomes richer in ammonia.

Potassium salts are only very slightly soluble, and in some cases evidently undergo decomposition with the ammonia nitrate.

Sodium salts dissolve to a small extent, or undergo decomposition, so as to yield a sodium compound in solution (sodium nitrate).

Ammonia salts are soluble or insoluble according to their nature. The behaviour of other salts, so far as the basylous radical is concerned, can be judged of by that of the chlorides.

Potassium chlorate is slightly soluble.

Nitrates are soluble salts; *potassium* slightly; *sodium* moderately; *silver* sparingly, the undissolved salt caking together; *lead* freely, the solution behaving like that of the chloride; and *barium* sparingly.

The *nitrites of potassium* and *sodium* are sparingly soluble.

Ammonia orthophosphate is almost insoluble, and is very slowly converted into a bulky substance (ammoniated ammonia phosphate ?).

Sodium orthophosphate is insoluble; so also is the *calcium* salt.

Sodium pyrophosphate is also insoluble.

Sodium metaphosphate is nearly insoluble.

Hydrogen metaphosphate is almost insoluble.

Borax slowly dissolves to some extent.

Ammonia sulphate is quite insoluble. Other sulphates are either quite or nearly insoluble, but are nearly all of them decomposed with the production apparently of insoluble ammonia sulphate. When ammonia nitrate contaminated with sulphate is treated with ammonia gas, the sulphate is left undissolved or non-liquefied.

Potassium sulphate is very slightly decomposed into ammonia sulphate, which precipitates, and potassium nitrate, which dissolves; a bare trace of the sulphate dissolves.

Sodium sulphate is slowly and superficially converted into a bulky crystalline substance, probably ammoniated ammonia sulphate. A trace of the sulphate dissolves and a little sodium (as nitrate).

Silver, *lead*, *magnesium*, *zinc*, *copper*, and *mercury sulphates* are apparently converted into ammoniated ammonia sulphate and more or less completely soluble ammoniated metallic salts.

Barium sulphate is insoluble.

Calcium sulphate is converted into prismatic crystals. Only minute quantities of calcium compound and sulphate dissolve. The crystals are probably an ammoniated calcium salt.

Manganous sulphate is converted into a very bulky substance. Only a trace of manganese dissolves and no sulphate.

Ferrous sulphate (obtained by heating the green sulphate nearly to redness in an atmosphere of hydrogen, and apparently pure) is converted into a very bulky substance of a light chocolate-brown colour. The liquid takes up a very little ferrous compound, but no sulphate. (The colour of the substance deposited is perhaps due to the presence of a little ferric salt: see *ferrous* and *ferric chlorides.*)

Alum is very slowly converted into a bulky substance. The liquid dissolves out a very little aluminic salt, which by water is thrown down as aluminium hydrate and a mere trace of sulphate.

Chromium alum instantly assumes a rich deep green colour, and very slowly imparts a rose-pink colour to the liquid, while a deposit of the same colour gradually forms. The liquid dissolves out potassium salt and a trace of sulphate. The deposit is soluble in water, and gives a violet-pink solution: this solution, or the pink liquid itself when mixed with water, may be boiled alone or with hydrochloric acid, without undergoing any change. Boiled with caustic soda, it loses its colour, and deposits a little chromic hydrate (see the chloride).

Potassium sulphite and *sodium hydrogen sulphite* are very slightly decomposed, and a trace only of sulphite passes into solution.

Ammonia chromate, yellow, crystalline, is converted into a much more voluminous, amorphous, yellow substance, quite insoluble in the liquid, but soluble in water. If not thoroughly dry, the chromate imparts a yellow colour to the liquid, but not otherwise; and even this disappears after a time by the deposition of all the chromium salt.

Ammonia anhydro or *red chromate* is very slowly converted into a yellow deposit, which is not voluminous as in the preceding case. The liquid is not coloured by the salt.

Potassium chromates, yellow and *red*, are slowly acted upon superficially, with the production of a yellow amorphous substance. The yellow chromate faintly colours the liquid, and both yield potassium salt to it. Although in the case of the anhydro chromates and of chromium trioxide (*vide supra*) ammonia chromate is probably formed, it is also evident the ammonia forms ammoniated ammonia chromate. A similar union appears to take place between ammonia sulphate and ammonia.

Lead chromate is converted into a bulky yellow deposit, which by water is reconverted into lead chromate. It hardly colours the liquid, but some lead dissolves.

Potassium permanganate readily dissolves, imparting its splendid colour to the liquid. A very gradual formation of gas soon commences and continues for a day or two, the liquid changing at the same time in colour and becoming deep yellow-brown. The liquid when of this colour is still transparent, but gradually yields a brown deposit and becomes of a fine dilute indigo tint. This shade of colour, lastly, slowly passes into a bright purple colour, which appears to be permanent. In this state the liquid is found not to contain much manganese; its bright colour is spoiled by water and discharged by acids. The brown deposit, on treatment with water, swells up into a bulky flocculent matter, presumably manganic hydrate. Potassium permanganate dissolved in ammonia-water is entirely decomposed in some hours; but in the presence of ammonia nitrate, which by itself is inactive, the permanganate is much more rapidly decomposed by the ammonia-water—probably because of the production, at first, of ammonia permanganate by the nitrate.

Potassium carbonate gradually disappears, some potassium nitrate taking its place. In consequence of the destruction of some of the ammonia nitrate, the liquid becomes surcharged with the ammonia, which has lost its solvent, and effervesces copiously. The liquid contains some potassium salt and some carbonate.

Sodium carbonate behaves like the potassium salt, but to a very limited extent. A similarly marked difference in intensity has been already indicated as marking the action of potassium and sodium hydrates.

Calcium carbonate is not acted upon.

Ammonia carbamate is moderately soluble.

Ammonia oxalate is quite insoluble.

Ammonia acetate (moist crystals dissolve freely).

Benzene, *oil of turpentine*, *indigo*, *strychnine*, *wax*, and *olive-oil* are insoluble.

Cane-sugar, *gum-arabic*, *litmus*, *tannin*, *phenol*, and *aniline* are soluble.

Gelatin is converted into a flocculent substance.

Butyric ether is slightly soluble without decomposition.

Methyl iodide is insoluble, but is slowly decomposed. Gas escapes, which is probably methylamine.

Ether is insoluble, but it causes the decomposition of the liquid, the ammonia bubbling through the ether, and the nitrate depositing.

Chloroform dissolves to a small extent, and separates again unaltered on the addition of water.

10. The liquid compound of ammonia nitrate and ammonia is a good electrolyte. With two BUNSEN'S elements hydrogen gas is freely evolved at the negative electrode, and one third of its volume of nitrogen gas at the positive electrode, as in the electrolysis of aqueous solution of ammonia. Large quantities of ammonia gas escape along with these gases by diffusion, so that the electrolysis appears to take place much more rapidly than it does do in reality. The loss of ammonia causes deposition of ammonia nitrate to occur, but a great difference is observed between the quantities of it deposited at the two electrodes. At the positive electrode, where the escape of gas is *less*, the nitrate soon begins to precipitate and also to crust the surface of the liquid; while at the negative electrode, where the escape of gas is *greater*, the nitrate does not appear for some time, and then only slowly,—that is to say, ammonia nitrate accumulates at the positive electrode, and ammonia itself at the negative one. The electrolysis of the nitrate and the secondary decomposition of the ammonia accounts for the above phenomena: for $H_4N \, . \, NO_3$ being resolved into NH_4 and NO_3, ammonia and hydrogen are set free at the negative electrode, while NO_3 appears potentially, though not actually, at the positive electrode, where it enters into reaction with ammonia to form ammonia nitrate and nitrogen, thus:—

$$3NO_3+4NH_3=3NO_3\,NH_4+N,$$

the N being equivalent to the H_3, which appears simultaneously at the negative electrode.

No reduction of the nitrate to a less oxidized salt takes place at the negative electrode. This is a fact of some interest, because it is opposed to the hypothesis that a *nascent* body possesses a chemical activity not belonging to it in its ordinary free condition; for here is basylous hydrogen, at the moment of its liberation, exerting no action on the nitrate, although zinc and other metals so readily reduce it under various conditions, including that of its solution in ammonia*.

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* Ammonium amalgam also appears to have during its decomposition no reducing action upon a nitrate, a fact, however, which may be due to the amalgam not being really a compound of ammonium.

When the positive electrode is formed of *platinum* or *iron*, it is unacted upon during the electrolysis; but when it is formed of *silver*, *mercury*, *lead*, *copper*, *zinc*, or *magnesium*, it is corroded, and no nitrogen is evolved. The silver, lead, and copper electrodes readily dissolve as nitrates, the copper one soon becoming coated with an azure-blue deposit. Mercury dissolves only slightly, but its surface becomes covered with a grey deposit. Zinc and magnesium dissolve as nitrates, but somewhat more slowly than the other metals mentioned, a fact probably to be accounted for by their tendency to direct or local action upon the nitrate.