

ART. LIII.—*Ammonia a constant contaminant of Sulphuric Acid*;
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IN reflecting upon some of the reactions by which ammonia is known to be formed, it occurred to me that this substance would very probably, or perhaps necessarily, be produced in the ordinary process of making sulphuric acid, and that it might remain as a contamination in the acid as used in the chemical arts. Acting upon the idea I have myself tested and have caused to be tested carefully and methodically a considerable number of samples of sulphuric acid obtained from different chemical works, and have found that every one of the specimens examined contained appreciable quantities of ammonia. I find, moreover, on looking the matter up, that the observation is not new, inasmuch as Schœnbein* has stated, so long ago as 1862, that he found traces of ammonia in all the samples of oil of vitriol which he had tested for that substance. My experiments would nevertheless seem to be worthy of publication, both because they confirm Schœnbein's statement and because they go to show that ammonia is far more generally distributed as an impurity of chemical substances than has been commonly supposed hitherto.

The following acids were examined quantitatively by distilling a small portion of each of them with milk of lime, free from ammonia, and applying Nessler's reagent to the distillate, in the manner described by Wanklyn, in his "Water-Analysis," London, 1874.

- I. Oil of vitriol from a carboy bought at Bay-Side Alkali Works, South Boston.
- II. Oil of vitriol from the Chemical Works at North Billerica, Mass.

* Wagner's Jahresbericht Chem. Technologie, viii, 266.

- III. Oil of vitriol from Eaton's Chemical Works, South Wil-
 mington, Mass.
 IV. Oil of vitriol, "chemically pure," from Trommsdorff of Erfurt.
 V. Pan acid from the Works at North Billerica.
 VI. Pan acid from Eaton's Works.
 VII. Chamber acid from Eaton's Works.
 VIII. Chamber acid from the Works at North Billerica.
 IX. Chamber acid from the Merrimack Print Works at Lowell.

Five cubic centimeters* of the acid		Gave grams of ammonia (NH ₃).
No. I	-----	0·000150
" II	-----	0·000075
" III	-----	0·000245
" IV	-----	0·000095
" V	-----	0·000070
" VI	-----	0·000140
" VII	-----	0·000050
" VIII	-----	0·000158
" IX	-----	0·000090

Care was taken to procure the above samples of acids (excepting Nos. I and IV) directly from the works where they were made. Each of the specimens was kept in a full and tightly closed glass stoppered bottle until tested, and the portion tested was taken from the middle of the bottle. With the exception of Trommsdorff's acid (No. 4) all the samples are known to have been made from sulphur, i. e., not from pyrites. Several other samples of oil of vitriol of unknown origin were found to contain ammonia when tested qualitatively with Nessler's reagent, and with the even more delicate reagent of Einbrodt.† So too when applied, for the sake of control, to the distillate from acid No. 4 of the foregoing list, Einbrodt's test gave a very strong reaction for ammonia.

There are several ways in which sulphuric acid may be contaminated with ammonia. Some insignificant traces of this substance are of course contained in the air which is used for making the acid, and a still larger amount is often contained in the water that plays so important a part in the process of manufacture. It is not impossible indeed that nitrogen compounds in the water may sometimes be the cause of appreciable traces of ammonia in the acid. It is easy to conceive moreover that considerable quantities of ammonia may be formed in the apparatus of the sulphuric acid maker through reduction of nitric acid or other oxide of nitrogen that is necessarily present,

* The weight of 5 c. c. of the oil of vitriol was rather more than 9 grams in each instance; that of the pan acid was about 8½ grams, and that of the chamber acid rather more than 7 grams.

† Mercuric chloride in alkaline solutions. See Liebig & Kopp's *Jahresbericht*, 1852, v, 723 and 1863, xvi, 167.

and I find, in fact, by direct experiment, that ammonia is formed when warm dilute nitric acid is made to act upon lead or upon sulphur.

Action of dilute Nitric Acid on Lead.—A quantity of soft, clean commercial lead that had just been remelted was placed in a small glass flask and 50 c. c. of dilute nitric acid (sp. gr. 1.15) were poured upon it. The flask was closed against the air with a gas delivery tube, and after the action of the acid had ceased the solution was boiled with the milk of lime and the distillate tested for ammonia. But the reaction with Nessler's liquor was so strong that no estimation of the amount of ammonia could be made. A quantity of the lead (30 grams) boiled by itself in the milk of lime gave a distillate in which no ammonia could be detected by the Nessler test. On the other hand, 50 c. c. of the dilute nitric acid were found to contain 0.000025 gram of ammonia.

In a second trial 50 grams of the commercial lead were warmed during three hours with 50 c. c. of the dilute nitric acid. The solution was distilled with the milk of lime and the ammonia in the distillate was estimated by titration with standard oxalic acid:—0.002483 gram of ammonia was found.

In a third trial 25 grams of pure lead (from Marquart of Bonn,) were warmed with 50 c. c. of the dilute nitric acid and 0.003279 gram of ammonia was found in the solution of nitrate of lead.

Action of dilute Nitric Acid on Copper.—15 grams of clean copper clippings were gently warmed with 50 c. c. of the dilute nitric acid until there was no more action. The solution was distilled with milk of lime, and the ammonia estimated by Nessler's test. 0.00004 gram of ammonia was found.

Action of dilute Nitric Acid on Sulphur.—20 grams of powdered brimstone were added to 50 c. c. of the dilute nitric acid and the mixture was maintained at or near the temperature of boiling for three hours. On testing the liquid an abundance of ammonia was found.

In another trial, 20 grams of the powdered brimstone were mixed with 100 c. c. of the dilute nitric acid. The mixture was allowed to stand in the cold for 48 hours, and then boiled gently during 8 hours. On testing the liquor by the Nessler process 0.00225 gram of ammonia was found in it.

A small amount of nitrogen oxides may perhaps be reduced to ammonia in the process of sulphuric acid making by other deoxidizing agents, such as the organic impurities of crude sulphur,* or sulphuretted hydrogen,† or even by sulphurous acid, though in a single experiment in which sulphurous acid,

* See Wagner's *Jahresbericht Chem. Technologie*, x, 149.

† Compare Johnston, in *Gmelin's Handbook*, ii, 396.

evolved from copper clippings, was passed into dilute nitric acid (sp. gr. 1·15) for a couple of hours no ammonia could be detected in the liquid. The experiment of Schönbein* moreover is to be remembered, in which ammonia, as well as sulphurous and sulphuric acids, was detected in water above which sulphur had been burned in the air. It would seem to be plain, however, that the substances previously mentioned must usually be the most efficient agents for the production of the ammonia.

Doubtless a good deal of the ammonia thus formed by reduction is destroyed again by reacting upon oxides of nitrogen in the liquid during the process of concentrating the weak sulphuric acid. Pelouze proposed long ago† to free the acid from nitrous contaminations by heating it with sulphate of ammonia. The reaction, though efficient, is simply incomplete.

The presence of ammonia in sulphuric acid having been proved, the question presents itself whether, in spite of the tendency of ammonia to change to nitrous and nitric acid through oxidation, traces of it may not occur in a great variety of the chemicals in whose preparation sulphuric acid takes part. The following list comprises several substances, chosen somewhat at random, which I have caused to be tested for ammonia, some of them for the sake of proving this idea, though mostly for a different purpose. The substances under examination were boiled with milk of lime that had been proved in each instance to be free from any trace of ammonia by long continued boiling, and testing of the distillates obtained from it. The distillates obtained after the addition of the substance to the lime were received in graduated tubes and tested successively with Nessler's reagent until they ceased to show any coloration.

	100 grams (or c. c.) of the substance contained gram of NH_3 .
Nitric acid, taken from a carboy of pure acid from Bay- side Alkali Works, 10 c. c. gave 0·000035 gram of am- monia (NH_3).	0·00035
Chlorhydric acid, the ordinary concentrated commercial acid, 10 c. c. gave 0·000015 gram of ammonia,	0·00015
Ditto from a carboy of pure acid from Bayside Alkali Works, 10 c. c. gave very little ammonia,	still less than the preced- ing.
Acetic acid, chemically pure, from C. White & Co., Philadelphia, 10 c. c. gave no reaction for ammonia, . .	0·00000
Potash alum, pure from Marquart of Bonn, gave strong reaction for ammonia,	much.
Ditto, pure from Trommsdorff, gave strong smell of am- monia when heated with lime. There was so much ammonia that it could not be estimated by the Nessler test, when 10 grams of the alum were operated upon, .	much.

* Journ. prakt. Chemie, lxxxvi, 145.

† Gmelin's Handbook, ii, 183.

	100 grams (or c. c.) of the substance contained gram of NH_3 .
Sulphate of alumina, pure from Marquart, 20 grams gave too much ammonia to be measured by the Nessler process (as used by us), and so did 5 grams, -	much.
Sulphate of iron (ferrous sulphate), 5 grams purified, from Powers & Weightman of Philadelphia, gave 0.00062 gram of ammonia, -	0.01240
Ditto, common copperas, the last of an apothecary's barrel, 5 grams gave 0.00507 gram of ammonia, -	0.10140
Ditto, copperas of unknown origin taken from a bottle in store room of Bussey Laboratory, 100 grams gave only 0.00053 gram of ammonia, -	0.00053
Ditto, a sample of pure sulphate of iron from Marquart, gave a strong reaction for ammonia when tested qualitatively, and a reaction was obtained also from a sample of Marquart's sulphate ("pure by alcohol,")	
Sulphate of lime, pure precipitated, from Marquart, 35 grams gave 0.0002 gram of ammonia, -	0.00057
Other samples of sulphate of lime, tested in a slightly different way, gave the following results:—545 grams of ground gypsum, obtained originally at a seed store but kept in a store-room of the Bussey Institution for a year or more, were percolated with pure water (two liters) until no reaction for ammonia could be detected and the percolate was boiled without addition of lime, 0.00392 gram of ammonia was found in the distillate. On adding lime a new portion of ammonia equal to 0.00008 was given off, -	0.000734
20 grams of ground gypsum bought at a seed store and tested immediately on reaching the laboratory, gave 0.00003 gram of ammonia on being boiled in pure water, and no more ammonia came off on adding milk of lime, -	0.00015
150 grams of plaster of Paris, taken from a box in the Bussey store-room, gave 0.0035 gram of ammonia on being boiled with water alone, and 0.00002 gram more of ammonia came off on boiling with lime, -	0.00234
20 grams of plaster of Paris taken from a keg found standing in a recently built house, gave 0.000035 gram of ammonia on being boiled with water alone, -	0.000175+
Sulphate of potash, chemically pure, from Trommsdorff, 20 grams gave only a faint trace of ammonia, -	trace.
Sulphate of soda, chemically pure crystals from Marquart, 20 grams gave no trace of ammonia. This result was verified by many qualitative trials, -	0.00000
Bisulphate of soda from Marquart, gave strong reaction for ammonia when tested qualitatively, -	much.
Sulphate of copper, pure from Marquart, 10 grams gave 0.000105 gram of ammonia, -	0.00105

	100 grams (or c. c.) of the substance contained gram of NH_3 .
Nitrate of potash, pure crystals from Marquart, 20 grams gave 0.000015 gram of ammonia,-----	0.000075
Nitrate of soda, taken from a bag of the crude nitrate of commerce, 20 grams gave 0.00004 gram of ammonia,	0.00020
Common salt taken from middle of a large lump of native rock salt bought at a grocer's shop, 20 grams gave 0.000022 gram of ammonia. Compare Vogel's detec- tion of chloride of ammonium in rock salt (Gmelin's Hand-book, ii, 416),-----	0.00011
Ditto, pure from Marquart, 20 grams gave 0.0000425 gram of ammonia,-----	0.000213
Ditto, a sample prepared by dissolving pure crystals of carbonate of soda in pure chlorhydric acid gave no reaction when tested directly with Nessler's reagent, -	none.
Phosphate of soda, pure crystals from Marquart, 20 grams gave no reaction for ammonia,-----	0.00000
Acetate of soda, pure crystals, 20 grams gave no reac- tion for ammonia,-----	0.00000
Carbonate of soda, pure crystals from Marquart, gave no reaction for ammonia when tested directly with Nessler's reagent,-----	0.00000
Carbonate of potash, pure from Marquart, gave no reac- tion when tested directly,-----	0.00000
Hydrate of soda, pure from Marquart, 5 grams gave no reaction for ammonia,-----	0.00000
Hydrate of lime, obtained by slacking the excellent quicklime from Brandon, Vt., 20 grams of the whitest portion of the mass gave no reaction for ammonia, while 20 grams of the grayest portion gave 0.00001 gram of ammonia,-----	0.00005
Chlorate of potash from Marquart gave 0.0001 gram of ammonia,-----	0.00050
Crude sulphur, from a box in Bussey store-room, 10 grams gave 0.00015 gram of ammonia,-----	0.00150
Flowers of sulphur from Marquart, 10 grams gave 0.00075 gram of ammonia,-----	0.00750
Sulphide of sodium from Marquart, 5 grams gave 0.001 gram of ammonia,-----	0.02000
Sulphide of potassium from Marquart, 5 grams gave 0.0009 gram ammonia,-----	0.01800
Sulphide of iron from Marquart, 5 grams gave 0.00085 gram of ammonia,-----	0.01700
Ditto, from a quantity of the foregoing that had just been fused in a Hessian crucible, 20 grams taken from the middle of the solid cake, gave 0.00025 gram of ammonia,-----	0.00125

Portions of the distillates from the sulphides of sodium, potassium and iron, on being tested with Einbrodt's reagent, for the sake of control, gave strong reactions for ammonia.

In order to avoid any confusion that might arise from coloration of the Nessler reagent by sulphuretted hydrogen, the following modifications of the ordinary process were employed in testing sulphur and the sulphides. In the case of sulphide of potassium and sulphide of sodium, the weighed substance was dissolved in about half a litre of pure water, free from ammonia, the solution was distilled and a quarter litre of distillate was collected, experience having shown that all the ammonia in the sulphide came forward in this amount of liquid. The distillate was acidified with a few drops of sulphuric acid, boiled until sulphuretted hydrogen had ceased to come off and then redistilled with milk of lime, the ammonia in the new distillate being determined with Nessler's reagent in the usual way.

In the case of sulphur and sulphide of iron the finely powdered, weighed substance was distilled with milk of lime, the distillate was acidified and boiled to expel sulphuretted hydrogen and finally redistilled in the manner just described.

Oxalic acid, "tertium depuratum" from Marquart, 20	
grams gave 0.0003 gram of ammonia,	0.00150
Tartaric acid, from Marquart, 10 grams gave 0.0001	
gram of ammonia,	0.00100
Vogel (Wagner's Jahresbericht, ix, 526) found 0.012 per	
cent of ammonia in a sample of crude tartar,	0.01200
Boracic acid, pure from Marquart, 10 grams gave 0.000055	
gram of ammonia,	0.00055;

that is to say, rather less than might have been inferred from the fact that ammonium compounds accompany boracic acid in the Tuscan lagoons (see Gmelin's Handbook, ii, pp. 97, 98; Bechi, Wagner's Jahresbericht, ix, 355; Vohl, *ibid.* xii, 205, and *ibid.* (N. S.) i, 210.)

Though the figures in the foregoing table may seem small or even insignificant to persons unaccustomed to use Nessler's test, they are really large in several instances and noteworthy in all. It should be understood, moreover, that in working with Nessler's process it is easy to exclude ammonia from the water and from the other reagents that are employed and to avoid the ammonia of the air. It is hardly necessary to urge that the utmost care has been exercised in these respects in all the foregoing tests. A large proportion of the substances tested were taken from the tightly closed, particularly well-ground, glass-stoppered bottles in which they had been imported and which had never been opened until the time of applying the test, but it is noteworthy that this precaution seemed to be devoid of significance.

Those substances, such as sulphate of soda for example, which contained no ammonia when taken from freshly opened bottles, likewise contained none when taken from bottles that had been frequently opened and which had stood in a store-room with other chemicals during three or four years. I find naturally enough, that filter paper and other porous materials that have been exposed to the air of a laboratory are highly charged with ammonia, in the same way that the reagent bottles upon our shelves become coated with ammonium compounds, but it would seem, nevertheless, that there is a limit to the penetrative power of the ammoniacal gases. It will be noticed for that matter that a tolerably large proportion of the substances examined contained no ammonia whatsoever, and in general I have not observed that chemicals taken from their bottles at the moment of reaching the laboratory are any more liable to be free from ammonia than those which have been long in store.

A good idea of the relative importance of the ammonia found in the chemicals above described may be got by contrasting the figures given in the table with the amounts of ammonia that occur in natural waters as given by Wanklyn and by many other authorities, or by comparing the above results obtained from chemicals with the following statement of results that were obtained from rain water in this laboratory at the same time and by the same operator.

One litre of rain water taken from
south cistern of Bussey Inst.

	Contained milligrams of Free NH_3 .	Albumenoid ammonia.	100 c. c. of the water contained grams free NH_3 .
April 20, 1875,	·532	·08	0·0000532
April 20, 1875,	·532	·06	0·0000532
April 22, 1875,	·480	----	0·000048
May 4, 1875,	·500	·10	0·00005
June 7, 1875,	·480	----	0·000048
June 7, 1875,	·475	----	0·0000475

One litre of rain water caught in
dish on roof of Bussey Inst.

July 23, 1875,	·100	----	0·00001
July 29, 1875,	·300	----	0·00003

One litre of rain water from
snow caught

April 20, 1875,	·147	·06	0·0000147
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It is worthy of mention that water obtained by melting ice—such as sold hereabouts, as in all American towns, for domestic use—is remarkably free from ammonia. Thus a litre of water obtained by melting a block of Muddy Pond ice was found to contain only ·013 milligram of ammonia. In other words, 100 c. c. of the melted ice contained no more than

0.0000013 gram of ammonia. A litre of water obtained by melting the clear portion of a block of Jamaica Pond ice, contained .04 milligram of ammonia, and a litre of water obtained by melting the cloudy porous portion of the same block yielded precisely the same amount, viz: at the rate of 0.000004 gram of ammonia in 100 c. c. of the water. By distilling off from a glass vessel a comparatively small proportion of the melted ice it is easy to expel these traces of ammonia and to obtain water that is practically free from that substance, such as is needed for making the standards of comparison upon which the Nessler test depends. It appeared in fact that before such distillation the mere melted ice was as free from ammonia as the water of deep wells in this neighborhood, that had been slowly boiled down in a copper still to four-fifths of its original volume for the express purpose of expelling ammonia. Both the melted ice and the purified well waters had to be distilled anew in glass vessels in order to obtain water that was completely free from ammonia, but the proportion of impure distillate to be thrown aside was no larger in the one case than in the other.

I am indebted to my assistant, Mr. D. S. Lewis, for his skillful coöperation in this research, and to my friend Mr. F. P. Pearson, chemist of the Merrimack Print Works, for a number of samples of acids.

Bussey Institution, Jamaica Plain, Mass., September, 1875.