

be in the direction of the least resistance; hence the movement of the ice in this lake is to the south.

In the forepart of last December I placed one end of a long pole against a tree on the low bank. The other end resting on the ice, where I made a mark. The temperature was 20° above zero in the morning, and rose to 40° by three o'clock P.M. during the day. The ice had moved toward the shore twelve inches. For several days the mercury indicated from 26° to 28° above zero in the morning, and rose to 35° or 40° during the day, and the ice would move out from six to eight inches, and at night would contract or draw back about one-fourth as much as it had expanded. Some mornings the thermometer stood below zero, and would run up to 15° or 20° above; still there would be the same outward movement. The same movement occurs, only to a less extent, when the mercury rises from 25° below zero to zero. These observations have clearly established the fact that the ice expands or moves outward when the thermometer is rising, and contracts or draws back when the temperature is growing colder. There is no outward movement of the ice on the north shore. There are a number of places on the south side where there are no springs, and the ice carries up in its frigid grasp the sand and gravel of the shallow bottom and sides, and piles them ten to fifteen feet high; and when the ice melts in the spring, the debris form a ridge, or adds to the height and width of one already formed, which are often 200 feet wide at the base—plainly showing that this work has been going on for ages. During the expansion of the ice, it cracks in thousands of places in all directions. When the weather turns colder, each separate piece of ice contracts, and the cracks open, the water rushes up and fills them and freezes, thus forming new ice to replace that which was left on the shore. Some scientists contend that the expansion of the ice is caused by the addition of new ice on the under side of that already formed. Actual observations refute that idea. Last winter the ice remained twenty inches thick for weeks, during which time there was a large outward movement of the ice every day. I made two and three daily observations nearly every day during December and January, and part of February. While the ice is expanding or contracting, there is a continuous cracking of the ice, the sound of which is almost deafening, and can be heard a mile or more.

The ice has averaged about twenty feet thick, and is so clear that fish can be seen in the water below. The cracks can be easily traced in the clear ice—some will be from top to bottom, others from the top part way through; while a few appear to begin at the bottom and come nearly to the top. This peculiar phenomenon is accounted for in this manner: The ice rests upon water which always remains at about the same temperature, 32° above zero. If the weather above is colder, the top of the ice contracts the most, forming cracks, which are widest at the top in the shape of a V. These fill with water and freeze. When the temperature rises above 32°, the top of the ice is expanded more than the bottom, which forces cracks in the bottom in the shape of the letter A, which fill with water and freeze. Thus, at every change of temperature, there are additions of new ice to replace that which has been crowded out on the shore. During this winter the total outward movement has been about forty feet over and above the contractions.

The movement of the ice last winter was more active than usual, for there was no snow to protect it from the weather. Snow is such a good non-conductor, that a covering of eight or ten inches will prevent any movement, and the ice will lie still all winter.

The breaking of a pitcher or other frail vessel, when water is frozen in it, is not caused by the expansion of the ice. The water freezes on the outer sides, first forming an unyielding and hermetically tight case around the water. The water thus inclosed is gradually frozen, and each particle or crystal of ice, as it is formed and forced into the confined water, takes up more room than the water did of which it is composed. It is like forcing hard substances into a barrel full of water until the pressure is great enough to burst the barrel. If there was a small hole kept open for the escape of the compressed water, there would be no harm done to freeze water in the most fragile vessel.

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Maine Prairie, Stearns Co., Minn., May 9, 1882.

ON THE PRECIPITATION OF TANNIC ACID AS TANNATE OF COPPER,*

As a supplement to my method of tannic acid determination, I have prepared this paper, which is a part summary of the results found while investigating the accuracy of the method. A tannate of copper was prepared from two sources, and examined in the manner noted below, not to demonstrate the hypothetical constitution, or to argue upon the much disputed subject, but merely to demonstrate the complete precipitation of the tannic acid from the decoction before the second titration, and to show its purity. I hope, however, that some chemist may investigate upon the hypothetical tannates, and by original research, and make known to us some of the compositions of this compound. If I had leisure at this time, I would investigate them myself, but as I am situated now this is impossible; however, I will attend to it in time. In reading up all that has been published upon tannic acids, I have become, as others, convinced that there is a wide field for research among the tannic acids and their tannates (that is, if there be more than one tannic acid, which I very much doubt). Summaries of results of the investigations of chemists upon this subject are innumerable, and have quite exhausted their merit by too frequent repetitions, so I will not mention them.

A pure tannic acid was prepared by dissolving the C. P. tannin of commerce in water, filtering, evaporating cautiously, and with additions of acetic acid, to dryness, washing the residue with absolute alcohol to remove gallic acid to prevent drying, dissolving in ether containing some water, and separating it from this by evaporation, drying finally in the air bath at a low heat; the product was pure and white. A solution was prepared holding four grammes of it to a liter of water, and was precipitated after rendering slightly alkaline with ammonia, by a ten per cent. solution of ammonio-sulphate of copper; the precipitate was allowed to settle, then transferred to the filter, and well washed with water containing a minute quantity of ammonia; it was then heated and dried at eighty-five degrees C. in the protected air bath; a portion of it was examined for ammonia, with negative results, no nitrogen compound being detectable; two portions were then taken of 0.5 gramme each; one of them was dissolved in acidulated water, and the copper precipitated with hydric sulphide; the precipitate was dissolved after a thorough washing with both hydric sulphide water

and water in nitric acid, etc.; this last was displaced with sulphuric acid, and the copper precipitated as metal, of which there was 11.68 grms., equal to 0.1386 gm. oxide, or 27.719 per cent.; the other portion was burnt, and yielded a formula, $C_{12}H_{10}O_{11}$, with three equivalents of cupric oxide.

It was in black lustrous masses, quite insoluble in cold water, but partly soluble in hot or boiling water, from which it is mostly deposited on cooling in alcohol gallic acid solutions, and in presence of alkalies quite insoluble. It is readily soluble in water acidulated with a mineral acid, but is precipitated unaltered on neutralizing the acid. For the other determination about 100 grammes of hemlock bark was taken and boiled with the decoctions, when cooled was filtered, and some dilute sulphuric acid added to the filtrate, which was again filtered, and the tannic acid precipitated from this filtrate exactly as above. The wet analysis yielded 0.1108 gm. copper, or 0.13773 gm. oxide, or 27.58 per cent., showing it to contain about 99.5 of tannate of copper as compared with the above, the combustion showing the same formula also, the figures differing by a small part. By these results we may readily observe that the tannate of copper formed is quite pure, and all the tannic acid is precipitated, thus setting aside all questions of inaccuracy of the method. Gallate of copper was prepared, and was found to be readily soluble in presence of free ammonia and acids, and quite insoluble in water; also that there is no double compound of gallic and tannic acid with copper.

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ON THE SEPARATION OF ALUMINA AND IRON FROM MANGANESE WITH AMMONIA.*

By NELSON H. DARTON.

The method proposed by Rose some years ago† for this separation is this:

"The solution sufficiently diluted and acid is mixed with some chloride of ammonium and heated to boiling. A fair excess of ammonia is added, and the mixture kept boiling gently for some time until all excess of free ammonia is expelled. It is then filtered, and the iron and alumina oxides on the filter thoroughly washed, the manganese remaining in solution in the filtrates and washings. If the quantity of manganese present was small, the precipitate contains hardly weighable traces of it. If, however, much is present, the precipitate is redissolved, and the above precipitation repeated."

This method has been frequently used by chemists generally, in this and other separations, its only fault lying in the fact that when a large proportion of manganese, a fair portion of alumina, and a little iron are present, it is difficult to obtain the precipitate free from manganese at the first treatment and reprecipitation, and thus leads us to use another method, saving us this inconvenience. Noticing the proportional discrepancies arising in this method, and wishing to find the point of maximum freedom of the precipitate from manganese, I investigated the process, and have prepared this table, showing the influence of the different proportions of the oxides of these three elements upon the proportion of manganese present in the precipitate. Compounds differing by 25 per cent. were taken, and the results are tabulated in per cents of the three oxides, sesqui-iron, alumina, and proto-manganese.

Iron.....	75	0.75	75	75	50	50	50
Alumina..	20	0.10	5	0	40	25	0.10
Manganese	5	0.15	20	25	10	25	40
1st Precip. Mn....	0.82	1.03	2.16	2.00	0.64	2.7	4.27
2d do....	none	mere trace	small trace	0.04	none	little	0.09
Iron.....	50	25	25	25	25	0	0
Alumina..	0	50	25	75	70	75	50
Manganese	50	25	50	0	5	25	50
1st Precip. Mn....	2.3	2.24	4.24	5.32	4.9	1.93	3.03
2d do....	0.43	trace	0.11	0.145	0.106	none	0.43

These figures were obtained all under the same conditions as regards temperature, etc. Although they show no connection with each other, show that when over 40 per cent. of manganese is present in a compound, it had better be separated by some other method, one bringing into use an acetate, under which conditions the iron, etc., can be separated without contamination. However, Dr. Waller tells me that the conditions are about the same in this method, but in a modified degree.

TO DISSOLVE SILVER FROM SILVERED ARTICLES.

COLD BATH.—For dissolving silver in the cold, the objects are hung in a large vessel fitted with the following mixture: sulphuric acid, 66° Baume, 10 parts; nitric acid, at 40° Baume, in which they remain for a greater or less length of time, according to the thickness of the coat of silver to be dissolved. This liquid, when it does not contain water, dissolves the silver without sensibly corroding copper and its alloys; therefore, avoid introducing wet articles into it, and keep the liquid perfectly covered when not in use. As far as practicable, place the articles in the liquid so as not to touch each other, and in a vertical position, so that the silver salt will fall to the bottom. In proportion as the action of the liquor diminishes, pour in small and gradual additions of nitric acid. Dissolving silver in the cold is regular and certain, but slow, especially when the proportion of silver is great. The other more rapid process is then resorted to.

HOT BATH.—Nearly fill a flat pan of enameled cast-iron with concentrated sulphuric acid, and heat to a temperature of from 300° to 400° Fahr.; at the moment of using it, pinches of dry powdered saltpeter are thrown into it, then hold the article with copper tongs in the liquid. The silver rapidly dissolves, and the copper or its alloys are not sensibly corroded. According to the rapidity of the solution, more or fewer pinches of saltpeter are added. All the silver has

been dissolved when, after rinsing in water and dipping the articles into the cleansing acids, they present no brown or black spots—that is, when they appear like new metals. These two methods are not suitable for removing the silver from wrought and cast iron, zinc, or lead; it is preferable to invert the electric current in a cyanide bath, or to use mechanical processes. Old desilvering liquors become green after use; to recover the silver, they are diluted with four or five times their volume of water; then add hydrochloric acid, or common salt. The precipitation is complete when the settled liquor does not become turbid by a new addition of common salt or by hydrochloric acid. The resulting chloride of silver is separated from the liquid either by decantation or filtration, and is afterward reduced to the metallic state by one of the methods which will be described.

FIXATION OF ALUMINA AS A DISCHARGE ON INDIGO-BLUE BY MEANS OF ALUMINUM CHLORIDE.

By G. SAGET.

THE property of hydrated aluminum chloride to be decomposed into alumina and hydrochloric acid when dried, may be used for obtaining a discharge on indigo blue, while alumina is deposited where the chloride has been printed, and may serve as a mordant for various colors. On adding manganese peroxide to the aluminum chloride, Scheele's reaction is obtained upon the tissue, the nascent chlorine destroying the coloring matter and producing whites. This reaction requires the presence of water and a temperature of 100°. The aluminum chloride must be perfectly neutral. To prepare it alumina is thrown down from aluminum sulphate by means of ammonia. It is collected upon a filter, washed, and dissolved in pure hot hydrochloric acid, taking care always to have an excess of alumina. The clear liquid is decanted and evaporated until a crystalline layer forms on the surface. The chloride is then of a sirupy consistence, and partially crystallizes on cooling. When it is to be used the crystals must be thoroughly mixed with the supernatant liquid. As for the manganese peroxide it is preferable to use that formed by the action of chloride of soda upon a salt of manganese, washing, and drying at 100°. The commercial peroxide contains too much impurities. The product thus obtained is reduced to an impalpable powder. The following discharge is then printed upon a medium indigo blue:

Manganese peroxide	80 grms.
Aluminum chloride.....	300 "
Calcined starch	200 "
Water.....	420 "

After printing, the pieces are steamed without pressure for an hour and a half, letting the vapors escape. There is obtained thus a design which is of a pinkish white, and which is cleared by a passage through weak hot hydrochloric acid. If the alumina is intended to serve as the mordant for a color the pieces are washed in hot water, then in cold water, and dyed. In this manner the author has obtained upon indigo blues fine designs in alizarin reds, fustic, or quercitron yellow, coerulein greens, etc. The discharge above given is intended for a medium blue; for a light or a dark shade it must be let down or strengthened in proportion.

A precaution to be taken when preparing this discharge is to add the aluminum chloride last, otherwise there are formed clots very difficult to get rid of. The peroxide and the calcined starch are first mixed, then the water is added, and when the paste is very smooth the aluminum chloride is stirred in by degrees. This discharge keeps well for a long time in a cool place. Manganic oxide may be substituted for the peroxide, but to obtain the same quantity of chlorine, a double proportion of aluminum chloride is preferable. Hence, from an industrial point of view, the peroxide is preferable.

Lead peroxide gives with aluminum chloride an analogous reaction. The author has sought to prepare a mixture such that after steaming and a passage through a chromate a yellow discharge would be obtained. Unfortunately, such discharges do not keep, and are completely useless after the lapse of a few hours. The contact of the copper rollers decomposes them at once, lead chloride and alumina are precipitated, and hinder the action of the doctors. The result is the same if red lead is employed.—*Moniteur Scientifique.*

ARTIFICIAL INDIGO.

PROF. ROSCOE writes in the *Journal of the Society of Chemical Industry*, No. 1, Vol. I.: "As supplementing the information on this interesting subject contained in my lecture delivered at the Royal Institution in May last, I have now the pleasure of adding the following particulars of Professor Baeyer's observations on his visit to the manufactory of artificial indigo in November last. This shows that the production of artificial indigo is making progress; and I may add that the manufacture is being carried on up to the present day in the manner described by him. It appears, however, that the consumption of propiolic acid is at present limited to a few print works, whose chemists have successfully overcome the difficulties of its application. Let us hope that the great majority of English calico printers will soon follow in the wake of the pioneers. The important question referred to by Professor Baeyer in his letter, viz., that of finding a useful employment for para-nitro-cinnamic acid, now a waste product in the manufacture of propiolic acid—may possibly receive a solution from the recent researches of Otto Fischer on the synthesis of the rosaniline dyes, by means of para-nitro-benzaldehyde, a body obtained by the limited oxidation of para-nitro-cinnamic acid. Another point which requires attention is the loss of material incurred in the passage from propiolic acid to indigo. If this loss can be avoided, and if a use is found for the para acid, there seems no reason why indigo blue should not be itself obtained in course of time by Baeyer's reactions, particularly as cinnamic acid can now be made in any quantity, and at a very low price.

"That these researches are only the first steps in the production of colors from the indigo group of compounds is shown by the fact that Professor Baeyer, in February last, patented the production of another coloring matter, termed by him 'indoin.' This resembles indigo in color, and is obtained by the action of concentrated sulphuric acid upon ortho-nitro-phenyl-propionic acid, when isatogenic acid is formed, and this is converted into the coloring matter by the action of ferrous sulphate. The soluble sulphurous acid compound of indoin is remarkable, and may become useful as a dye."

The following extracts from Professor Baeyer's letter will

* Read before the American Chemical Society, Feb. 3, 1882.

† *Pogg. Annal.*, 110, 304 307.