When heated the precipitate became white and was in fact molybdic anhydride. As ammonium phosphomolybdate is much less soluble in dilute nitric acid containing ammonium nitrate than in dilute nitric acid alone, we considered it possible that the excess of ammonium nitrate might be the cause of the instability of these solutions and an experiment showed this to be the case. We found that the solution prepared according to the following formula remained practically unaltered for several months and gave exactly the same results as a fresh solution when used for the determination of phosphorus in steel. The following is the formula and method of preparation:

One hundred grams of molybdic anhydride was thoroughly mixed with 400 cc. of cold distilled water and eighty cc. of ammonia (0.91 sp. gr.) was added. This completely dissolved the molybdic acid. The solution, after filtering to remove any silica or dirt, was poured into a mixture of 300 cc. nitric acid (1.42 sp. gr.) and 700 cc. water. The solution did not become very warm and there was very little tendency on the part of the molybdic acid to separate out during the mixing.

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THE FERRATES.[1]

BY CLAUDE A. O. ROSELL.

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"WHO has first seen ferric acid?" This question forms the pertinent title of a controversial article in the *J. Prakt. Chem.*, **32**, 448, and it is there stated that G. E. Stahl discovered that when saltpeter is ignited with iron and the mass is added to water, the caustic alkali resulting from the decomposition of the saltpeter holds a part of the iron in solution and produces an amethyst or purple color. He also stated that if dilute solutions of iron in nitric acid are poured in successive small portions into a strong solution of caustic potash the iron is dissolved on shaking, with a blood-red color.

While verifying the accuracy of the former I have not been able to reproduce the latter of these reactions. On its face it

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[1] Read at the Brooklyn meeting.

looks so improbable that it must be believed that the statement is erroneous. Probably the nitric acid that Stahl used contained sufficient hydrochloric acid to make the reaction possible. Be this as it may, certain it is that the direction given by Stahl for making potassium ferrate in the dry way, through the ignition of saltpeter with iron, is sufficiently clear to be successfully followed, so that he is undoubtedly entitled to the credit of being the discoverer of ferric acid.

As recently as in Muir & Morley's edition of Watt's Dictionary of Chemistry, London, 1889, page 547, it is stated that "Stahl noticed in 1702 that a violet solution is obtained by fusing iron with saltpeter and washing with water or by adding a solution of iron in HNO_3 to conc. KOH aq.," which shows that these two editors had nowhere found a correction of the erroneous statement of Stahl, nor has a correction been published by any one until now.

In 1802 potassium ferrate was rediscovered by Ekeberg, while fusing gadolinite, which is a silicate of yttrium, beryllium, and iron, with caustic potash. In this experiment the ferric oxide, of which the gadolinite contains sixteen per cent., was oxidized in the presence of caustic potash so as to form potassium ferrate. However, neither Stahl nor Ekeberg examined the character of the iron compound which resulted from the reaction with the caustic potash, either added or produced in the process, and which gave rise to the claret color observed.

When Fremy undertook an investigation of those compounds of the metallic oxides, in which the latter play the part of acid metallic anhydrides, he very soon rediscovered the solution of ferric oxide in caustic potash. In this solution he found that the oxide did not exist as ordinary ferric oxide, Fe_2O_3, but that it contained more oxygen than the latter, the quantity of oxygen contained corresponding roughly, or as closely as it was possible to analytically determine the constitution of an impure and somewhat variable body, such as barium ferrate, to the formula FeO_3, a result which has since been confirmed by J. Denham Smith and H. Rose.

The accounts of Fremy's work were published from time to time in a number of scientific periodicals, commencing with

January, 1841, when he states that the compound of oxide of iron and potash which is soluble in water corresponds in composition to the manganates, and in 1842 the new compound was called by him ferric acid, though the name had already been suggested by J. Denham Smith in Phil. Mag. Ser. [3], **19,** 302.

Besides producing potassium ferrate by the methods of Stahl and Ekeberg, which were unknown to him, Fremy also obtained it by electrolyzing caustic potash with an anode of cast iron and also by introducing chlorine into a solution of caustic potash containing ferric hydroxide in suspension. In addition he produced this salt by heating iron with potassium dioxide.

In attempting to produce sodium ferrate by such processes as Stahl and Ekeberg had used to produce potassium ferrate he failed. Not only did Fremy fail in his attempts to produce sodium ferrate in the dry way, but there is not to be found in the literature of the subject any account of anybody else who has succeeded in doing so or who has ever suggested the possibility of its being accomplished. In fact the statement occurs in chemical literature that sodium ferrate cannot be made except in the wet way. Thus in Wurtz' Dictionnaire de Chimie, Volume 1, Part 2, page 1413, the following is found: "Sodium ferrate is soluble in water and cannot be prepared except in the wet way."

Bloxam prepared a solution of sodium ferrate by adding bromine to a strong solution of caustic soda containing ferric hydroxide in suspension. This I have found a very quick and convenient method of producing a small quantity of a solution of sodium ferrate. I have also several times made the attempt to produce sodium ferrate by the addition of iodine to a solution of caustic soda holding ferric hydroxide in suspension, but no sodium ferrate was formed.

Bloxam also found that a solution of calcium ferrate may be produced by gently heating a solution of bleaching powder with a small portion of ferric chloride. On repeating this experiment I have found the process to be a very delicate one and that it often fails, although, if very carefully conducted a rose-red solution of calcium ferrate is formed. I thought that perhaps by the addition of lime to the bleaching powder solution the reaction might take place more expeditiously. Such, however, was not the case, as a solution of calcium ferrate could never be produced when lime was first added to the bleaching-powder solution containing a small portion of ferric hydroxide in suspension.

It was first stated by Fremy and it has subsequently been repeated in the text-books that calcium ferrate, like barium ferrate, is insoluble in water. The experiment of Bloxam above referred to shows that this statement is not correct.

On preparing a solution of sodium or potassium ferrate allowing it to stand, it sometimes changes color from red to green. J. Denham Smith believed this green solution to be caused by some new iron compound, but Heinrich Rose showed that it was derived from manganese. The ferrate solution prepared contained a manganate. On standing, the ferrate decomposed while the manganate remained unchanged until at last only manganate remained, when the solution turned green. I have repeatedly verified the correctness of Rose's explanation.

In undertaking a course of investigation of the properties of ferric acid the following interesting problems presented themselves:

1. Production of sodium ferrate in the dry way.
2. Production of iron dioxide.
3. Decomposition of barium ferrate by metathesis so as to obtain in this way a normal ferrate containing no free alkaline hydroxide.
4. Determination of the constitution of the thioferrates.

I. PRODUCTION OF SODIUM FERRATE IN THE DRY WAY.

In the attempts to produce sodium ferrate in the dry way, ferric oxide, both dry and hydrated, was calcined with caustic soda, sodium carbonate, sodium nitrate, and with mixtures of sodium hydroxide and nitrate, and also with sodium nitrate and carbonate, but all in vain. The substitution of sodium chlorate for a part or all of the sodium nitrate was also tried but with no change in the result. Sodium dioxide was then tried, but at first without success. It was however observed that when the fused mass from this last experiment had been allowed to cool, on subsequent addition of water it became highly heated, and it was suspected that while sodium ferrate had been produced by the reaction, that it was at the same time decomposed by the heat, resulting from the addition of the water, and it was believed that if this rise in temperature could be obviated the decomposition of the ferrate might be prevented. This theory was acted on and the mass resulting from the fusion of the ferric oxide and the sodium dioxide was treated with ice, and though some rise in temperature still followed it was much less than before, and sodium ferrate was obtained in solution. Thus the first problem had been successfully solved and sodium ferrate was for the first time produced in the dry way. There are two probable reasons why Fremy failed. In the first place, when using sodium nitrate this was to a great extent decomposed by the heat leaving behind sodium nitrite which is stable at high temperatures, and which, when the mass was dissolved in water served as a reducing agent, reducing the iron trioxide to the ordinary ferric oxide, while the nitrite itself, by oxidation, became converted into nitrate. When using caustic soda the cause of the failure was probably the heating of the mass on the addition of water, which heating has already been referred to.

II. ATTEMPTED PRODUCTION OF IRON DIOXIDE.

The production of iron dioxide was of course the most important of the problems. The hope of accomplishing this result was the inciting cause of the investigation and a great number of experiments were conducted with this end in view.

As it is well known that chromium dioxide can be readily obtained by adding a solution of a chromic or chromous salt to a chromate it would seem at first sight that, having the iron monoxide and the trioxide, the iron dioxide might be easily prepared by an analogous reaction to the one above mentioned.

To produce a precipitate of iron dioxide from a solution of sodium ferrate, which is highly alkaline, the solution of the iron salt added would have to be alkaline. Such a solution may be made in many ways, such as by the addition of tartaric acid, citric acid, or glycerol, to a solution of a ferric salt and then adding a caustic alkali in excess, but in each case the organic solvent was oxidized before any precipitate was formed and so this method had to be abandoned.

The addition of barium ferrate to solutions of ferric chloride, both normal and basic, was tried with apparently good prospects of success as the barium went into solution as chloride, but at the same time oxygen and also chlorine were given off, so that the precipitate ultimately obtained consisted merely of ordinary ferric hydroxide. For the purpose of this experiment, the barium ferrate was just as good as normal sodium ferrate could this latter be produced; the barium ferrate decomposed the ferric chloride perfectly, so that if iron dioxide is capable of production, here the conditions of success seemed to be the best and yet the result of the reaction was only ordinary ferric oxide. Hence, it is quite certain that if iron dioxide can be made at all, it is a compound of such exceeding instability as to have decomposed as fast as formed.

III. THE REACTIONS OF BARIUM FERRATE.

Of the ferrates the most stable, the one that can be prepared in the purest state and the most definite in composition is barium ferrate, $BaFeO_4.H_2O$, this formula having been determined by Fremy and H. Rose. Before barium ferrate has been allowed to dry it is decomposed by all the soluble acids, including carbonic acid. After it has once been allowed to dry in a desiccator it is not so easily decomposed, at least completely. If barium ferrate, which has not been allowed to dry, be suspended in water through which carbon dioxide is passed, it will be completely decomposed with the formation of barium carbonate and ferric hydroxide, oxgen being set free. From this decomposition it might reasonably be expected that iron dioxide would be formed just as manganese dioxide is formed on passing carbon dioxide through water containing barium manganate in suspension, but such is not the case. This experiment would also seem to indicate that neither a compound of iron, corresponding to a permanganate nor a compound corresponding to a bichromate exists. The result of passing carbon dioxide through water containing barium ferrate in suspension, with the object of obtaining new iron salts therefore carries with it two disappointments.

When barium ferrate has been thoroughly dried in a desiccator it is readily attacked by acids, but complete decomposition is not readily effected in the cold even with dilute sulphuric acid, oxalic acid, formic or acetic acids. Hydrochloric acid decomposes it completely with the greatest readiness, chlorine being always set free. If barium chromate be digested with a solution of sodium ferrate, barium ferrate is formed and the solution changes color from red to yellow, due to the sodium chromate which has been formed. The reverse reaction never takes place. Thus, if barium ferrate is digested with a cold solution of an alkaline carbonate, sulphate or triphosphate, an alkaline ferrate is never formed, the solution remaining colorless. An alkaline sulphate will decompose barium ferrate that has not been dried with the formation of barium sulphate and ferric hydroxide, oxygen being set free. It thus appears that barium ferrate is one of the most insoluble salts known. It is strange that in none of the publications up to this time has the behavior of barium ferrate to neutral salts been referred to.

IV. THIOFERRATES.

Fremy states that on passing hydrogen sulphide through a solution of sodium ferrate a solution is obtained of a beautiful emerald color. He supposed that the sodium ferrate was converted into sodium thioferrate. On passing hydrogen sulphide through a solution of sodium ferrate I sometimes obtained the green solution described by Fremy and at other times not. Investigating the matter, I found that the green solution was obtained only when the original solution contained manganese. It appears then that on passing hydrogen sulphide through a ferrate solution containing a manganate the ferrate is reduced by the hydrogen sulphide, leaving the green manganate solution behind. If, on the other hand, the ferrate solution contains no manganese, on passing hydrogen sulphide through it, the red color disappears and a solution is obtained having a greenish yellow tinge, such as is obtained by digesting precipitated iron sulphide in a solution of an alkaline polysulphide, the greater part of the iron being precipitated as black sulphide. The supposed thioferrates must therefore be considered as mythical.

The only use so far suggested for the ferrates, is the production of oxygen described in British Patent, No. 85, Jan. 10, 1886, to Brooman, a communication by Maréchal and Tessie du Motay, in which it is stated that potassium, sodium, and barium ferrate may be decomposed by a current of steam and subsequently reformed by the action of a current of air at high temperature.

Whether the ferrates resemble the chromates or manganates more is difficult to say. If a salt could be produced corresponding, either to the bichromates or the permanganates the question would of course be immediately decided. The extreme insolubility of barium ferrate, together with the solubility of calcium ferrate, as well as the instability of the dioxide, if it does exist, brings the ferrates closer to the chromates than the manganates. On the other hand the soluble ferrates can only exist in alkaline solutions, and in this respect they resemble the manganates. In their oxidizing power the ferrates still more closely resemble the manganates. It has already been stated that a ferrate will oxidize nitrites, tartrates and glycerol. The soluble ferrates are also decolorized or reduced by oxalates, alcohol, ether, ammonia, urea, and other soluble organic bodies with very few exceptions, such as, and notably, the acetates. They are decomposed also by some insoluble organic bodies, such as paper and insoluble carbohydrates, but most insoluble organic bodies, such as the paraffines and benzene, decompose them but very slowly.

To perform all the experiments on ferrates above referred to, sodium and potassium ferrate had often to be prepared. Of all the methods of making these salts the easiest is to pass chlorine through a strong solution of sodium hydoxide, containing ferric hydroxide in suspension. At one time I produced sodium ferrate on a scale never before attempted. Three kilos of sodium hydrate were dissolved in enough water to form ten liters of solution. To the solution were added 150 grams of ferric chloride, and the mixture stirred for a long time until the ferric hydroxide formed was all finely divided and evenly distributed throughout the solution. Through the mixture chlorine gas was then passed from a cylinder of liquid chlorine which had kindly been presented by my friend Dr. Rudolph Knietsch, one of the leading chemists of the Badische Anilin und Soda Fabrik of Ludwigshafen. Germany. The operation was carried on very successfully, the chlorine gas passing through with great regularity, and in this manner a quantity of stock solution was prepared sufficient for all subsequent experiments.

It may here be stated that whenever an experiment is described above it has been actually tried for the purpose of making sure that the reaction indicated actually takes place.

The following is a summary of the errors which occur in the literature of ferric acid:

1. The direction for making potassium ferrate by adding iron nitrates to caustic potash, by Stahl.

2. The statement that on standing a solution of potassium ferrate changes color and turns green, made by J. Denham Smith.

3. The statement that calcium ferrate is insoluble in water, made by Fremy.

4. The direction for making thioferrates by passing hydrogen sulphide through a solution of a ferrate, by Fremy.

5. The allegation that sodium ferrate cannot be made except in the wet way, made by Wurtz.

Of these, the second error was corrected by H. Rose and the third by Bloxam, the other three having now for the first time been brought to light.

In the annexed bibliography are included only original articles, and when articles have been reprinted in different periodicals, only the first has been given. The full titles of the articles referred to have been perused, so that it is certain that they exist and relate to the subject-matter indicated.

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[CONTRIBUTION FROM THE LABORATORY OF THE LOUISIANA SUGAR EXPERIMENT STATION AND SUGAR SCHOOL.]

A SIMPLE AND CONVENIENT APPARATUS FOR ESTIMATING THE WATER-HOLDING POWER OF SOILS.

BY J. L. BEESON.

Received June 3, 1895.

TO a fifty or 100 cc. plain burette is connected a glass Y tube by means of a piece of rubber tubing. To one of the forks is attached a bit of rubber tubing carrying a pinch-cock, and the other fork is connected with a small Stutzer extraction tube, having a zero mark scratched on its neck, by means of a stout piece of rubber tubing about two and one-half feet long. The apparatus is fastened in the clamp of an ordinary clamp-stand. A metallic disk, which will about fit the larger tube, is perforated with many small holes, the center with a larger hole that will admit the end of a piece of glass tubing, which is made firm by