XIII.—*On the Tests for Nitrates, and a new one for Nitrites.*

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My attention having been directed to the detection of nitric acid in cases where, if it existed at all, its quantity could be but small, I deemed it necessary, as a preliminary step, to ascertain the merits of some of the tests usually adopted for that purpose. The experiments were confined chiefly to two reactions, generally considered the most

susceptible for nitrates; the one where the indication of the presence of nitric acid is the production of a dark violet or brown colour, caused by adding a solution of protosulphate of iron and concentrated sulphuric acid to a solution of a nitrate; the other, where it is the destructive action of nitric acid on indigo, the solution of the nitrate being made slightly acid with sulphuric acid, and then a solution of sulphate of indigo added. Before, however, detailing the results I have arrived at with respect to these tests, I shall proceed to describe a new one that has suggested itself for nitrites, but which admits, under certain circumstances, of application also for the detection of nitrates. Thinking that the addition of dilute hydrochloric acid to a solution of a nitrate in presence of iodide of potassium and starch-paste, might cause the chlorine thus liberated to act in the nascent state on the iodide, and so produce the well-known blue colour, I tried the experiment and found it to answer apparently most successfully. I was, however, surprised to find that of several nitrates employed, that of potassa was the only one with which the experiment succeeded; furthermore, that hydrochloric acid was not at all a necessary condition for the production of the blue colour, oxalic, dilute sulphuric, and even diluted nitric acids effecting the same, whilst the same diluted acids produced no change in a simple mixture of iodide of potassium and starch-paste. It was therefore evident that the action was not dependent on chlorine, but on some substance to be found in nitrate of potassa, and which will be demonstrated by the following experiments.

On distilling a few grains of nitre dissolved in five ounces of water with a small quantity of concentrated sulphuric acid, a distillate was obtained of slightly acid reaction, which when neutralised with carbonate of potassa and concentrated, and then added to a mixture of iodide of potassium, starch-paste, and dilute hydrochloric acid, was found to produce a much deeper blue colour than did a concentrated solution of the original nitrate. This led me to try the effect of the nitrites on the same test-mixture, and which I found to possess the property of liberating iodine under the circumstances described in a most remarkable degree, and which must be attributed to the reduction of hydriodic acid by nitrous acid. On subjecting the nitrate of potassa employed for the foregoing experiments to recrystallisation, the crystals then obtained were found to have entirely lost the property they originally possessed, whilst the mother-liquor retained it in a high degree, clearly showing that the peculiar action of the nitrate of potassa was to be attributed to the presence of a small quantity of nitrite. It has been shown that a very distinct indication of

nitrous acid was obtained in the distillate from ordinary nitre and sulphuric acid; in order to see if such would be the case with small quantities of pure nitre when treated with pure sulphuric acid, I repeated the experiment, employing two grains of the pure salt, six ounces of water, and half an ounce of concentrated sulphuric acid, when, after treating the distillate in the manner before described, abundant proof was afforded of the presence of nitrous acid. In all cases, therefore, where distillation is necessary in searching for nitrates, this test may be indirectly applied for them. Those substances which interfere with the formation of iodide of starch under ordinary circumstances, prevent its production also by the present test. The method of employing the test is the following: A few drops of a dilute aqueous solution of iodide of potassium (free from iodate) are mixed with a little starch-paste, and then dilute hydrochloric acid of sp. gr. 1.006 added. The liquid suspected to contain a nitrite, if alkaline, must be slightly acidified with hydrochloric acid and then added to the test-mixture, when, if much nitrite be present, a dark-blue colour will be instantly produced; and if very small traces only, then the liquid first assumes a pale fawn colour, which gradually changes to that of violet, plum, and ultimately dark-blue. The extraordinary delicacy of the test will be seen from the following experiments. When water containing only the $\frac{1}{1,000,000}$ th part of nitrous acid (as nitrite of soda, $\text{NaO} \cdot \text{NO}_2$) is added to the test-mixture, a violet colour is almost instantly produced; with the $\frac{1}{1,500,000}$ th part, the colour makes its appearance in a few seconds; with the $\frac{1}{2,000,000}$ th part, after the lapse of two or three minutes; with the $\frac{1}{4,000,000}$ th part, a change may be observed in twelve minutes, and with the $\frac{1}{5,000,000}$ th part, a violet tint is produced in about fifteen minutes. In all these cases, the liquid rapidly assumes a dark-blue colour. By performing the experiments in a porcelain basin, the faintest indication of colour may be observed. In searching for minute traces in a very large bulk of liquid, it is advisable to add more iodide of potassium than where the volume of the liquid is small. Since performing these experiments, I find that Schönbein* has noticed the action of nitrites on iodide of potassium.

With respect to the tests for nitrates specified at the commencement of the paper, De Richemont† has found that by the employment of the first one, he was able to detect the $\frac{1}{24,000}$ th part of nitric acid in a solution. The one by means of indigo has had narrower limits assigned to it; Liebig‡ who suggested it, states that the $\frac{1}{200}$ th

* J. Pr. Chem. XLV, 227.

† Graham's Chemistry, 297.

‡ Gmelin's Handbuch der Chemie, I, 813.

part of nitric acid may be recognised by it, and the $\frac{1}{500}$ th part, when a little chloride of sodium is added. I shall endeavour to show, that in both cases the action is in all probability due to nitrous acid, contained either originally in the substance as nitrite, or produced by the action of sulphuric acid upon the nitrate; at any rate, that nitric acid in the cold has no apparent action upon either of them. And first, as regards the test with sulphate of protoxide of iron. If sulphuric acid be added to a solution of nitrate of potassa free from all nitrite, and briskly agitated with it, so as to prevent the mixture from becoming heated, and then a solution of sulphate of protoxide of iron added, no change whatever in the colour of the liquid will ensue, even when allowed to stand for some time, which could not be the case did the action of the test depend on nitric acid. If to the same mixture, one drop of a dilute solution of nitrite of potassa be added, a brownish colour will be immediately produced, showing the instantaneous effect of nitrous acid upon the test. If instead of keeping the mixture of nitrate of potassa and sulphuric acid cold, we gently warm it, and then add a solution of protosulphate of iron and a few drops more of concentrated sulphuric acid, a dark-violet colour will immediately appear, accompanied by an energetic disengagement of gas; the colour in this case soon disappears, owing to the heat evolved, but can readily be reinstated by a fresh addition of the protosulphate of iron. Or again, if we first add a solution of protosulphate of iron to the solution of the nitrate, and then pour in the concentrated sulphuric acid in such a manner that it forms a layer at the bottom of the vessel, we shall find that a violet colour will be produced at the contact-surface of the two liquids; the heat in this, as in the former case, being sufficient to cause the formation of nitrous acid. In searching, therefore, for small quantities of nitrates, it is advisable to add, as recommended by De Richemont, a large bulk of concentrated sulphuric acid. With respect to the delicacy of this test for nitrites, I have found that a liquid containing the $\frac{1}{8,000}$ th part of nitrous acid (in the form of a soda-salt) becomes immediately coloured green upon the addition of a small quantity of sulphuric acid and sulphate of iron; that perceptible shades of green are produced when a liquid contains the $\frac{1}{500,000}$ th, and a faint colorisation with the $\frac{1}{1,000,000}$ th part. In like manner to the preceding test, I have found that a solution of pure nitrate of potassa which has been treated in the cold with concentrated sulphuric acid, or decomposed with tartaric acid, has no action whatever upon a solution of sulphate of indigo, but that the presence of the smallest quantity of nitrous acid is sufficient to destroy the same. By applying heat to the mixture of sulphuric acid

and solution of nitre, to which a few drops of indigo-solution have been added, the colour of the latter will be found rapidly to vanish, and the test then becomes an exceedingly delicate one for nitrates, and in the absence of chlorates and organic matter, may be most advantageously employed for them. I have examined the delicacy of the test for nitrites, and have found that the one, two and three millionth part of nitrous acid in a solution may be detected by means of it.

By all the foregoing tests it will be found that the sulphuric acid of commerce, as well as most kinds of carbonate of potassa, contain a trace of nitrous acid. In conclusion, I may state that I have applied the nitrites to the detection of the iodides, the results of which experiments will be found in the accompanying communication.