ON THE CONDUCT OF FINELY DIVIDED IRON TOWARD NITROGEN.

By IRA REMSEN.

A RECENT writer* states that the method of Lassaigne for the detection of nitrogen in bodies containing carbon is not applicable to compounds in which sulphur is present. He claims that the sulphur gives rise to the formation of sulphocyanide, and that this is overlooked, as the solutions are strongly acid. A list of compounds is given in which nitrogen cannot be detected. It includes taurine, sulpho-urea, sulphocyanide of potassium, and the "amides of the sulphonic acids." In such cases it is recommended to fuse the bodies with sodium and pure iron, instead of sodium alone, as is customary. The sulphur forms sulphide of iron, and the nitrogen forms the cyanide and can easily be detected.

As I have repeatedly used the ordinary method for the detection of nitrogen in compounds containing sulphur, and have in some cases relied upon the results reached, I undertook an examination of the subject thus opened, and I have been led to conclusions directly opposed to those of the writer referred to. At the same time certain interesting observations have been made on the conduct of pure iron, reduced by hydrogen, toward nitrogen.

As regards the statement that the method of Lassaigne is not applicable to compounds containing sulphur, I am prepared to give this an unqualified denial. I have examined every one of the substances mentioned by the writer, with the exception of cystine, and have in each case without the slightest difficulty obtained the precipitate of prussian blue. I have also examined a large number of other substances, and have never experienced difficulty in getting the result looked for. Then, further, the fact that sulphocyanide of sodium or potassium itself breaks up under the influence of heat in the presence of an alkaline metal shows clearly that, even if this salt is formed as is claimed and as is probable, the detection of the nitrogen cannot be interfered with by the presence of sulphur.

Having shown beyond a doubt that the conclusion I had drawn with reference to a certain compound, that it contained no nitrogen, is correct, I nevertheless fused a small specimen of this compound with sodium and iron by hydrogen, and was astonished to find that, on extracting the fused mass with water, filtering, and then adding successively ferric and ferrous salts and hydrochloric acid, the blue precipitate revealing the presence of nitrogen was distinctly formed. I repeated the experiments a number of times, but always with practically the same result. In every case the blue precipitate was formed, though in some cases it seemed to be formed in larger quantity than in others. The variations in quantity were, however, not striking.

I now took other non-nitrogenous organic substances than the one which was in question and tested these. The two purest specimens in this laboratory at the time were one of the double tartrate of potassium and sodium which had been recrystallized a large number of times, and one of cane sugar which had been repeatedly recrystallized from alcohol. These two specimens may certainly be regarded as in the strictest sense chemically pure. Both of these substances gave the reaction for nitrogen distinctly. Of all the substances experimented upon, the pure double tartrate seemed to be best adapted to the purpose, and in continuing the experiments I have since always employed this particular pure specimen to furnish the carbon.

The question naturally suggests itself, whence comes the nitrogen in these reactions? I at first suspected the iron by hydrogen, and my suspicions were increased when, on inquiring into the history of the specimen used, I found that it had been made from ferric hydroxide precipitated by ammonia. To be sure the hydroxide had been washed with the greatest care, and had afterward of course been ignited in a current of hydrogen, and it did not seem probable that ammonia or any compound of ammonia and iron could be retained; but still, there was the nitrogen, and it appeared at least possible that it was actually contained in the iron. To test this point ferric hydroxide was precipitated from a solution of the pure chloride by means of sodium carbonate and washed out until no test for sodium could be obtained. This precipitate was then divided into two parts, one of which was dried at once, and the other boiled for some hours with a solution of ammonium carbonate and ammonia. The latter was then washed out, no special precautions being taken to remove all the ammonium salts, and afterward dried. Both specimens were separately reduced in a current of purified and dried hydrogen. Both gave the test for nitrogen, and indeed the one from which all ammonium compounds had been carefully excluded seemed to give the test better than the other.

Another specimen of iron by hydrogen which has been in the collection of chemicals for this laboratory for five years, and which does not take fire by contact with the air, failed to give the nitrogen test. This led me to think that possibly the nitrogen is not contained in the iron, but is absorbed from the air, and that the power to absorb nitrogen in this way is connected with the active condition of the iron. Both the specimens above referred to, which in the active condition readily and invariably gave the test for nitrogen, were allowed to stand for a short time in contact with the air and were then again tested. Neither gave the reaction. The same experiment was performed with the specimen of iron by hydrogen first used, and which had been preserved under ether. A portion of this was allowed to stand over night exposed to the air and then gave no indication of the presence of nitrogen. These results make it appear extremely probable that the nitrogen detected when active iron is used is really absorbed from the air. But if this is so, then more thorough contact of the heated reagents with the air ought to increase the quantity of cyanide formed. All the experiments thus far mentioned were performed in test tubes, and of course very little air came in contact with the substance at the bottom of the tube. On heating the necessary mixture in a crucible, however, violent combustion of the sodium took place and no reaction for nitrogen was obtained. To prevent this combustion, a mixture of iron by hydrogen, double tartrate of sodium and potassium and metallic sodium was placed in a hard glass tube, and dry hydrogen passed through while gentle heat was applied to drive off water. Then nitrogen was passed slowly over the mixture, while at the same time it was heated to redness. This process was continued for about ten minutes, when, on allowing the tube to cool, the contents were extracted with water, filtered, and treated in the usual manner. To my surprise, a very large precipitate of prussian blue was formed, much larger in proportion than in any previous experiment. The result is so striking that the experiment is well adapted to serve the purpose of a lecture experiment, illustrating the formation of cyanogen from the nitrogen of the air. There can be no

doubt that the nitrogen is really absorbed from the air. The quantity of the precipitate obtained in the last experiment was so great as to exclude the supposition that the nitrogen could have been present in the substances used. Then, further, the fact that the active iron, which readily gives the test for nitrogen, does not give the test after it has been exposed to the air and become oxidized, is a clear indication that the active condition of the iron is an important factor in the process, and that the nitrogen cannot be in combination with the iron. For, if it were, it is difficult to understand how the spontaneous oxidation of the iron could remove it. The heat evolved can scarcely be sufficient to decompose any nitrogen compound present, for the iron is heated to a much higher temperature in the course of its preparation, and the possible nitrogen compound must have been decomposed by this first application of heat.

I have thus far performed no quantitative experiments, and there are obvious difficulties in the way of making these exact. As it is intended soon to continue the experiments, however, an attempt will be made to determine as nearly as possible how much nitrogen can be taken up and combined chemically by given weights of the reagents. Some other points of interest will also be taken up. Thus, in attempting to exclude the air from the vessels in which the reactions took place, hydrogen was used, and the nitrogen test was not obtained. But on testing a nitrogenous substance (hippuric acid) in the same way, very little evidence of nitrogen was obtained. It would, hence, appear that the test cannot be applied in an atmosphere of hydrogen, or that the cyanide is decomposed when heated in hydrogen. On the other hand, Marchand* has stated that hydrogen does not interfere with the application of the test.

As a result of the experiments described in this paper, it may be stated with confidence that *when iron by hydrogen and certain non-nitrogenous organic substances are heated together with metallic sodium in an atmosphere of nitrogen, a cyanide is readily formed.* The action is, of course, similar to that which takes place in blast furnaces, and which gives rise to the formation of cyanide of potassium. In the latter case, the carbonate of potassium from the burning of the fuel furnishes the potassium. Nitrogen is always present in large quantity, and the iron is constantly passing from the state of oxide to that of the metal.

Marchand some years ago showed† that steel when heated with carbon and potassium can take up nitrogen. It had been previously stated by Schaffhäutl‡ that steel always contains nitrogen. The experiments of Marchand made this statement appear improbable though they did not disprove it. Indeed, later a discussion arose in France on the same subject. Fremy claimed that not only is nitrogen always present in steel, but it is the essential element of the steel. This discussion did not at the time lead to a satisfactory conclusion. Quite recently Müller§ has found nitrogen in not inconsiderable quantity in the gases extracted from Bessemer steel by boring, but thus far he has not been able to determine whether the nitrogen is simply inclosed in the pores of the steel or is chemically combined with it.

I have made a number of experiments with Bessemer steel and with other forms of iron, and have obtained results in accordance with those already on record. It seems possible that as regards steel the nitrogen detected may be partly absorbed from the air and partly present in combination with the iron, though it would be difficult to prove the correctness of this supposition.—*Amer. Chemical Journal.*

SPONTANEOUS IGNITION OF COAL.

By H. HAEDICKE.

RICHTER's experiments tend to show that the decomposition of coal in the presence of moisture depends on the pyrites, while the destructive action of oxygen occurs only at an elevated temperature, and is checked by the presence of moisture. The influence which pyrites may exercise on the decomposition of coal is of a twofold nature. It becomes first oxidized by the co-operation of moisture, and is transformed into ferrous sulphate; and during its formation the coal becomes split up and exposes a larger surface to the air; this ferrous salt is then oxidized into the ferric salt, which gives up oxygen to the coal.

These assumptions throw some light on the causes of spontaneous ignition, which are mainly attributable to the action of pyrites. The author found that pyrites ignites in pure oxygen at a temperature of about 200°. He attaches great importance to this subject, and gives some statistics as to the occurrence of accidents through spontaneous ignition—no less than 70 accidents were recorded among 31,116 ships in 1874 as resulting from this cause. To prevent spontaneous ignition, it is especially requisite to exclude all currents of air, unless the latter is passed through from the commencement in a strong current so as to act as a cooling agent. As moisture prevents ignition and accumulation of oxygen, it is desirable to introduce a jet of steam if there is any great increase of temperature in the coal.—*Dingl. polyt. J.*

OZONE.

EM. SCHOENE|| calls attention to the fact that, since the existence of hydrogen superoxide in the air has been demonstrated, the occurrence of ozone as a constituent of the atmosphere has become very doubtful. Most of the reactions formerly relied upon for the detection of ozone are also produced by hydrogen superoxide. The latter liberates iodine from the iodides and oxidizes thalious compounds. It does not oxidize manganous salts, but such oxidation cannot be regarded as an evidence of the presence of ozone, since ordinary oxygen in the presence of carbonate of ammonium—which is always to be found in the air—will effect it. The tarnishing of silver may be, and probably always is, due to the presence of sulphides. The odor sometimes observed and ascribed to ozone is at best a questionable argument for its presence. Most observers would be liable to confound the odors of ozone and hyponitric acid. Moreover, ozone is not produced by the electric spark in a mixture of oxygen and nitrogen, but only oxide of nitrogen, hence the fact of visible electric discharges in the air is no evidence of its formation. It is produced by the silent discharge, but of this, as an atmospheric phenomenon, we still know too little to justify us in regarding it as a probable source of supply.

* Journal prak. Chemie, 49, 355.

† Loc. cit.

‡ *Ibid.*, 19, 409.

§ Berichte deutsch. chem. Gesell., 14, 1.

|| Berichte d. deutsch. chem. Gesell.—*Amer. Chem. Jour.*

SYNTHESIS OF SALICYLIC ACID.

By EDGAR F. SMITH, of the Laboratory of University of Pennsylvania.

UPON heating one part of copper benzoate with about three parts of distilled water in a sealed tube at a temperature of 180° C., for a period of three hours, a large quantity of cuprous oxide separated. The contents of the tube were then removed to a rather large beaker, acidulated with hydrochloric acid, and the solution supersaturated with hydrogen sulphide. The filtrate from the copper sulphide contained, of course, a considerable amount of benzoic acid, which was removed by distillation in a current of steam. The residual liquid reduced to a small volume gave a crystallization of needles, fusing constant at 156° C., and afforded with ferric chloride the characteristic coloration given by salicylic acid. The salts also proved the presence of the latter. The reaction, then, described above may be graphically represented as follows:

The experiment repeated gave the same result. A quantity sufficient for analysis was obtained, although its separation from the benzoic acid was attended with difficulty. In one or two instances the method was slightly modified. An aqueous solution of benzoic acid and an ammoniacal solution of cupric oxide were employed. The mixture was heated as usual, but it was necessary to increase the temperature to 220° C. The yield of salicylic acid in either case was never very abundant.—*Am. Chemical Journal.*

ON A PURE COKE.

By W. W. STAVELEY.

I HAVE recently had occasion to test a sample of coke, made from coal-tar pitch, which I found to contain a very small percentage of sulphur. Since it is not generally known that coke of such purity is obtainable in large quantities, it may be well to record the analysis:

Sulphur.....	0.12	0.11
Ash.....	2.43	2.50
Carbon.....	97.45	97.39 by difference.

The sulphur was estimated by the prolonged boiling of the powdered coke, 5 to 6 grms., with nitric acid and a little chlorate of potash. The ash was estimated by heating for several hours in a Fletcher's muffle furnace at a white heat. The sample of coke was taken from the ovens and powdered while hot, thus insuring the absence of moisture. Several determinations of sulphur and ash were made with similar results. A noticeable feature of this coke is that on exposure to the weather, even for months, it does not "slack" or disintegrate. This is no doubt due to the small percentage of sulphur present, the cause of the slacking of most cokes—gas-coke especially—being attributable to the oxidation of the sulphides of iron contained in the coke. The heating and burden carrying power of this coke in the furnace far exceeds that of the best Durham coke. From its hardness and close texture it is especially calculated to resist the action of the hot gases on the upper portion of the furnace, thus diminishing the loss.—*Chem. News.*

SODIUM AND POTASSIUM CHLORIDES IN MINERAL ANALYSES.

By DR. FR. MUCK.

THE author remarks that these chlorides often accumulate to a serious extent and prove very inconvenient. He evaporates the filtrates containing magnesia (whether before or after the precipitation of the lime) almost to dryness, covers the residue with cold, fuming hydrochloric acid, stirs well, waits a few minutes, decants repeatedly through a filter formed of glass beads and cotton, and finally washes the saline mass upon the filter completely with strong hydrochloric acid. The residue obtained after evaporating the filtrate contains, in addition to magnesium chloride, very little fixed chlorides, and requires for its solution but a very small quantity of water. The use of glass beads containing lead must be carefully avoided, and also "glass wool," which apparently cannot be procured uncontaminated with lead.

OPHIOPHAGY.

THE KING SNAKE (OPHIBOLUS SAYI) SIPS ON A FULL GROWN WATER MOCCASIN (ANCISTRODON PISCIVORUS).—"Be ye therefore wise as serpents."—Matt. x. 16.

The non-venom secreting Ophibolus and the deadly Ancistrodon had kept a friendly companionship for several days in the same prison box. Well aware of each other's peculiar method of self-defense, there had been a policy truce instituted for the nonce. The former did not relish a hypodermic injection of poison from his surgeon neighbor, and the latter equally as much dreaded a fraternal embrace from his acrobatic companion. The one abhorred convulsions and tetanoid calisthenics as much as the other deprecated triturated ribs and macerated scales. The sky became suddenly changed, and such a change! etc., *vide* Byron. Without warning, the king snake instantly whipped a coil or two of its tail around the neck of his neighbor, just as the cracker of a whip doubles into a knot by the movement of the staff in the hands of a deft coachman. Before the moccasin could recover from the shock, its entire body was tightly pressed by the reduplicating folds of its agile enemy. From neck to tail and back again, its entire length was tied up so effectually that respiration became difficult, movement of the body was out of question, excepting a vibrating tremor passing helplessly from nasal tip to tail tip, and a swift contracting of the assailant's convoluting folds assured the victim of broken ribs and speedy helplessness. The mouth

* Berichte d. deutsch. chem. Gesell., 12, 2316.