XLVII.—*On the Existence of Nitrogen in Steel.*

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THE experiments which we are about to lay before the Society were undertaken with the intention of throwing some further light upon the vexed question, "Is nitrogen an essential constituent of steel;" and if so, of showing whether its presence in greater or less quantity could be held to account for the difference in quality of various kinds of steel.

In pursuance of these objects, we have repeated Frémy's experiments for the purpose of estimating the amount of nitrogen contained in different samples of both steel and iron, including *cast steel*, *blister steel*, and iron of the well known mark P , *Bessemer steel*, *specular iron* (*Spiegeleisen*), a kind of iron now used to a considerable extent for further carburizing steel during the ordinary process of refining, wrought iron of English manufacture, and the same converted into steel at a full red heat in a current of carbonic oxide.

The apparatus used in these experiments has been varied considerably during their progress, but the general plan of investigation has remained the same throughout, and the alterations have only been intended to secure more completely those conditions which were found to be absolutely indispensable to obtaining a correct result. Those conditions may be briefly stated as consisting either in the total exclusion of nitrogen, in whatever shape or form, from the apparatus and the gas used, or, as we found in some cases more satisfactory, in the employment of such a modification of the apparatus as would admit of our estimating what quantity of the nitrogen obtained was due to any sources other than the steel under examination.

The general method of experimenting was as follows—Hydrogen, purified, and more or less dried, was passed over the steel or other substance under analysis heated to full redness, and was then conducted into a Wills' nitrogen apparatus, where the ammonia generated by its passage over the red-hot steel, was absorbed in a standard solution of sulphuric acid, and its amount afterwards estimated by volumetric analysis. It was then of course easy to calculate the quantity of nitrogen contained in the steel.

In the first experiments, no means were taken specially to exclude or make allowance for the nitrogen that might be present as air, either mixed with the hydrogen in the gasometer, or in the tubes of the apparatus before the commencement of the experiment, reliance being placed in the former case upon the hydrogen being prepared with such care as to insure its purity, and in the latter, upon the gas being passed through the apparatus a sufficiently long time to sweep out the air previously contained in it before the experiment was commenced.

The above remarks apply more particularly to experiments No. 1 to 11 inclusive, in which the apparatus used consisted merely of—

1. Solution of potash.
2. Column of pumice wetted with sulphuric acid.
3. A U drying tube of chloride of calcium.
4. The analysis tube.
5. Will's nitrogen bulbs filled with standard acid.

The steel in all the experiments was used in the form of fine powder (passed through a muslin sieve), filings, grains (the size of ordinary shot) or strips, about 3 inches to 4 inches long, $\frac{1}{4}$ inch to $\frac{3}{8}$ inch wide, and about $\frac{1}{50}$ inch to $\frac{1}{100}$ inch in thickness. The passage of the gas through the potash-bulbs varied from the rate of 50 to 150 bubbles per minute, and was continued after the heat was withdrawn until the assay tube was cool. The following Table (No. 1) exhibits the result of the first eleven experiments just mentioned; by a reference to it, it will be noticed that in all these instances, except in No. 2, nitrogen was obtained, though varying in quantity, from .007 % to .068 %.

TABLE I.

No. of Expt.	Description and state of steel employed.	Quantity of steel.	Duration of Expt.	Amount of N. obtained.
1	β Blister steel, in grains..	50·000 grm.	1 hour	·068 per cent.
2	" "	25·000 "	2 "	·000 "
3	" "	25·000 "	2 "	·0293 "
6	" "	33·3345 "	2½ "	·020 "
7	Cast steel, in strips.....	37·93075 "	1½ "	·027 "
8	" "	18·6415 "	3½ "	·018 "
9	Bessemer-steel, in filings.....	50·000 "	2 "	·011 "
11	" "	55·723 "	1½ "	·007 "

These experiments we consider as preliminary ones only, and judging from the experience we afterwards obtained, must reject

altogether Nos. 1, 3, 6, and 7 as being incorrect, from the nitrogen obtained being, at all events in part, derived from other sources than the steel; most probably from some air remaining in the apparatus when the experiment was commenced; and when the comparatively large quantities of nitrogen obtained are taken into account, there can remain but little doubt that this source of error vitiated the results in all these instances.

Experiment No. 2 demands a special notice; it seems to have given what we must now look upon as an accurate result; however, as it was only the second experiment of the kind that we had made, we do not feel justified in laying any very great stress upon it, although, in referring to our note-book, we do not find any further reason to doubt its accuracy. In experiments Nos. 8, 9, and 11 the amount of nitrogen found has materially decreased. This may probably have arisen from the precautions requisite to insure an accurate result becoming better understood, and especially to extra care being taken in preparing the hydrogen, and in driving out the air from the apparatus more completely before commencing the experiments. We therefore consider these three entitled to more confidence than the preceding ones.

On comparing all these experiments generally together, however, a gradual but unmistakeable decrease in the amount of nitrogen was at once apparent. This appeared strange, and aroused a suspicion that possibly much, if not all of it, might be due to other sources than the substance under examination, and it was evident that more careful experiments were necessary to arrive at a perfectly correct result. It was therefore determined to try if the nitrogen present in the apparatus could not be entirely removed, so as to insure the hydrogen arriving at the assay-tube in a state of absolute freedom from this impurity. The best method of doing this seemed to be to convert it into ammonia, and to absorb it in this state by dilute acid; and the apparatus was accordingly modified thus:—

1. Flask containing potash as before.
2. Tube filled with soda-lime, at a red heat, and about six inches in length.
3. Dilute sulphuric acid.
4. Assay-tube.
5. Wills' nitrogen bulbs filled with standard acid.

The distance between the sulphuric acid and the steel was made as short as possible, with the view of reducing to a minimum

the quantity of air it would contain, and the further precaution was taken of passing the gas over the soda-lime for some time before the steel was heated. It will thus be seen that if any nitrogen was present, either in the hydrogen, or in the apparatus it would become converted into ammonia by passing over the soda-lime, which passing onwards would be absorbed by the sulphuric acid. There would now remain only the small space above the liquid in the sulphuric acid bottle, and the short and narrow tube between it and the assay-tube in which any air could lodge to vitiate the results.

With this arrangement, experiments 13 to 17 were made, Nos. 13 and 14 were made upon cast steel, in thin strips similar to those previously described, and Nos. 15 and 17 upon *specular iron* crushed to powder in a steel mortar and passed through a fine muslin sieve. It will be noticed by a reference to Table No. 2 that considerable quantities of these substances were used, but in only one case was any nitrogen detected. This was in No. 15, upon specular iron, but there seems to be some doubt respecting the accuracy of this experiment, for from a remark in our notebook it seems that the assay-tube was heated before the air was entirely expelled from it, and as in the subsequent experiments upon the same substance none gave any nitrogen whatever, it is probable that this or some other error must have crept in.

TABLE II.

No. of Expt.	Kind and state of substance employed.	Quantity used.	Duration of Expt.	Amount of N. obtained.
13	Cast steel in strips	27·081 grm.	1 hour.	·000 per cent.
14	" "	26·706 "	(?)	·000 "
15	Specular iron, in fine powder...	20·583 "	3 hours	·015 "
17	" "	20·000 "	1 "	·000 "

In all these experiments the gas issuing from the soda-lime tube was tested for ammonia by placing small pieces of reddened litmus-paper in the narrow tube leading from it into the sulphuric acid bottle. They invariably gave indications of its presence, and traces of it could be found even after the hydrogen had been passing through for more than an hour. The assay-tube was never heated until these traces had entirely disappeared.

In the next series of experiments that were made, the soda-lime tube was dispensed with, and no means were taken to absorb

the nitrogen in the apparatus. The hydrogen was prepared with every possible precaution however, and was passed direct from the gas-holder into the assay-tube, without any intervening apparatus, except a wash-bottle filled as full as practicable with a solution of protosulphate of iron, made slightly alkaline with potash. As short an apparatus as possible was used, and the hydrogen passed through it for a long time before heat was applied to the assay-tube, the object being to reduce the amount of air contained in the apparatus to the least possible quantity, and to sweep it out completely, so as to prevent the nitrogen it contained from interfering with the result. The protosulphate of iron was intended to absorb any oxygen that might be present, it being frequently found that the steel was slightly oxidised when the experiment was ended. It was replaced for experiments Nos. 51 and 52 by a solution of oxide of lead in potash. This was used to absorb hydrosulphuric acid, a small quantity of which was given off during some of the experiments.

This method was found to answer very well in practice, although of course open to the objections which have been stated before; very great care is however requisite in making the experiments, but when sufficient attention is given to them, it may be relied upon for giving correct results.

In Table No. 3 a detailed account of the experiments made with this arrangement is given. A glance at it will show that in the whole series we obtained no amount of nitrogen that could be considered of any importance, even with the possible chance of the errors we have previously pointed out, and we therefore submit that the negative results obtained in these instances are very strong evidence that nitrogen is not an essential constituent of steel.

TABLE III.

No. of Expt.	Kind and state of steel employed.	Quantity used.	Duration of Expt.	Amount of N. obtained
19	Specular iron in fine powder ..	7·190 grm.	0 $\frac{3}{4}$ hours.	·000 per cent.
20	Cast steel in strips	15·536 "	3 $\frac{1}{4}$ "	·000 "
21	Iron in strips	25·713 "	2 "	·0051 "
23	Cast steel in filings	14·6215 "	6 "	·000 "
24	" "	15·077 "	3 "	·000 "
35	" "	40·057 "	3 "	·0023 "
51	Steel made by heating iron in C.O.	8·005 "	2 "	·0015 "
52	Spiegeleisen in grains.....	80·000 "	4 "	·000 "

In three of the above experiments slight traces of nitrogen were discovered. Still the amounts are so very small that they cannot be looked upon as essential to the constitution of steel, especially when so many other experiments fail to show any trace whatever of nitrogen.

In the succeeding experiments, an important alteration was made in the apparatus, which requires a short description. Two tubes, one containing the steel to be operated upon mixed with soda-lime, and the other containing soda-lime only, were placed side by side in the same furnace, and heated to the same temperature, whilst the hydrogen was passed from the same gas-holder through both, the current being so regulated that an equal quantity passed through each tube in a given time. Previously to its entering the tubes, the hydrogen was washed by passing successively through a solution of hydrate of potassium and dilute sulphuric acid, and in some cases was partially dried by passing through concentrated sulphuric acid immediately before its entrance into the steel and soda-lime tubes. The first of these was made upon cast-steel filings, 6·355 grm. of which were taken and intimately mixed with 6·3 grm. of soda-lime, 6·3 grm. of soda-lime alone being placed in the second tube. Both were heated to a full red heat for $2\frac{1}{2}$ hours. No nitrogen was obtained. The whole of the series were made in a precisely similar manner, Nos. 25, 30, and 36 upon cast steel in filings, and Nos. 32, 33, 34, and 37 upon $\tilde{\text{P}}$, blister steel and iron of the same mark, also in filings. A reference to the following Table will show the results obtained:—

TABLE IV.

No. of Expt.	Quantity of steel employed.	Kind and state of steel employed.	Quantity of soda-lime mixed with the steel.	Duration of expt.	Amount of N. obtained.
25	6·355	Cast steel in filings	6·3	$2\frac{1}{2}$ hrs.	·000 per cent.
30	5·000	„ „ „ „ „	5·0	$6\frac{1}{2}$ „	·000 „
32	5·091	$\tilde{\text{P}}$ Blister steel in filings ..	5·0	$4\frac{1}{4}$ „	·000 „
33	10·117	„ Iron „ „	5·0	3 „	·000 „
34	9·980	„ Blister steel „	5·3	2 „	·010 „
36	21·0405	Cast steel in filings	15·0	2 „	·0009 „
37	19·456	$\tilde{\text{P}}$ Blister steel in filings ..	6·7	1 „	·0040 „

There is one remark to be made respecting the length of time that the steel was submitted to the action of hydrogen in these

experiments. It was invariably found that the greater part of the nitrogen, in those cases where any was obtained, was given off in the earlier part of the time, and that, in the latter part, no indication could be found. It appears very probable from this that in those instances the nitrogen was supplied by the air in the apparatus.

In judging of these experiments, it must also be borne in mind that if any of the samples of steel operated upon had contained nitrogen, the method of analysis could not have failed to show it, and therefore it cannot be said that it may have been present in cases where we have failed to detect it; whilst it is equally certain that any that might have been accidentally present in the apparatus would have been shown. Thus, in cases where nitrogen was obtained, every allowance for error must be made; whilst in those in which absolutely none could be detected, the results must be rigidly adhered to.

Having now given a full description of the methods of experimenting, we would next direct attention more particularly to the different kinds of steel and iron employed, and the quantity of nitrogen obtained from each.

Excluding, for the reasons previously given, the first five experiments, there are four made upon B blister steel, and iron. Of these two, Nos. 32 and 33, gave absolutely no nitrogen, whilst the others, Nos. 34 and 37, gave only $\cdot 004\%$ and $\cdot 010\%$, quantities which, in our opinion, were due to the sources of error before-mentioned. Taking the average, $\cdot 0036\%$ is obtained, an amount which is too small to be considered of any moment. These were all made upon the same sample in the state of filings.

Next follow ten experiments upon cast steel. These were made partly on cast steel in the form of strips, and partly as filings. In these a remarkable unanimity is observable in the results, for out of the ten, eight gave no indications of nitrogen whatever, and the other two only $\cdot 018\%$ and $\cdot 0023\%$. The average of the whole being $\cdot 0020\%$, an amount which may be considered as quite inappreciable in influencing the quality of steel in the slightest degree. Then come two experiments on Bessemer steel; both these show nitrogen, one to the amount of $\cdot 007\%$, and the other $\cdot 011\%$. In both these cases, large quantities (50 grm. to 55 grm.) were used, and it may be possible that this peculiar kind of steel contains some small quantity of

nitrogen ; though, even in this case, the nitrogen would not affect its quality, being most likely an accidental constituent, formed during the process of manufacture, from the stream of air driven through the molten iron forming some compound in it analogous to that which nitrogen forms with titanium, and which is so often found in crude pig irons.

Then follow four experiments upon specular iron, which show, with one exception, a total absence of nitrogen. One of these must be particularly alluded to, viz., No. 52, in which 80 grm. were submitted to experiment for four hours. At the end of this time it was found that no nitrogen whatever had been eliminated.

This we look upon as one of the best and most conclusive experiment we have made, and its evidence is very strong in favour of the conclusion that nitrogen is not essentially present in steel. The two experiments which remain to be mentioned were made upon iron of English manufacture, of very soft quality, and the same converted into steel by heating to full redness in a current of carbonic oxide. In both cases the result was so small as to indicate mere traces of no importance.

These are the experiments we have to lay before you, and, after reviewing the whole of them, the only just conclusion that can be arrived at is that nitrogen does not exist, either in steel or in iron, as an essential constituent, and cannot therefore be made use of to explain the different commercial qualities of those substances. Altogether there are twenty-two experiments, upon which we can fairly place reliance, as containing no manifest error, and of these thirteen gave absolutely no nitrogen. Of the remaining nine, six do not exceed one-hundredth per cent., and of the other three, one gives only eighteen, one only fifteen, and the remaining one no more than eleven-thousandths per cent. of nitrogen.

Taking the average of the whole, it amounts to but $\cdot 0033\%$, a result which we submit is practically of no value. The adhesion of air to the surface of the steel would be sufficient, in most cases, to explain the amounts which, in some instances, were obtained, and in experiments carried to such a nicety, this source of error must not be overlooked. This, and that arising from the air remaining in the apparatus, small as its amount may have been, are quite sufficient, in our opinion, to account fully for all the nitrogen obtained. It is not of course to be expected that in a long series of experiments, every one should be as successful as could be wished ; but we have laid these before you, good and bad,

as they occurred, rejecting only such as contained a manifest and palpable error, and from the whole we give it as our opinion, that nitrogen is not an essential constituent of steel or iron, that it very rarely exists in them even as an accidental constituent, and that it has nothing whatever to do with the respective qualities of different samples of those substances.

Without at all wishing to undervalue the researches of others, we may express a doubt whether the nitrogen they obtained in their experiments was not altogether derived from those sources of error we have pointed out, and which we ourselves found it difficult to guard against entirely. At the least we may state that, in our hands, the method adopted by M. Frémy for estimating nitrogen in iron has led to different results.