tion which finds its simplest and readiest explanation in the pushing back of the hydrolysis[1] by means of hydrochloric acid produced by the reaction, and in possible catalytic action of reaction products. In solutions free (or as free as possible) from acid this acceleration is so great that an actual increase in the rate of oxygen absorption occurs during the first part of the reaction. It soon appears, however, that although the results of any one series of measurements are consistent within themselves and in certain ways also the results of different series are consistent with one another (*i. e.*, the ratios of initial value to end value of velocity constants are very approximately constant), nevertheless the velocity constants for different series vary within very wide limits. This suggests the action of catalytic influences, and Part II is devoted to the detection and qualitative investigation of some of these catalytic agents. The way for further investigation is perfectly apparent. The first task will be to protect the stannous solutions from possible catalytic influences and to determine, if possible, the normal values for the velocity constants of the reaction with varying concentrations of hydrochloric acid, after which the influence of the various catalytic agents will be open to quantitative investigation.

The chief result of the work at present is, however, the development of an apparatus and a method by means of which reactions between liquids and gases may be readily and quantitatively studied.

The main portion of this work was carried out in the laboratory of the Physical-Chemical Institute, at Leipzig.

STANFORD UNIVERSITY,
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DETERMINATION OF SULPHUR IN WROUGHT IRON AND STEEL.

BY GEORGE AUCHY.

Received January 22, 1901.

SEVEN or eight years ago in four samples of high carbon steels sent to two firms of commercial chemists (same drillings to each) for analysis, the sulphur was reported as follows :

	Sample No. 1.	Sample. No. 2.	Sample No. 3.	Sample No. 4.
Chemists A	0.013	0.015	0.012	0,015
" B	0.002	0.001	0.003	0.002

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[1] Kortright (*Am. Chem. J.*, 17, 116) has called attention to the probable influence of hydrolysis in the reaction between $SnCl_2$ and $FeCl_3$.

These results are interesting as illustrating the meagerness of our knowledge of our methods just a few years ago ; results such as these go to justify the sarcasm of the iron-master, who some years back declared that Ananias was the father of chemists.

In the light of our present knowledge it is easy to guess that the results of Chemists B were obtained by the aqua regia method. At that time it was customary to precipitate by the addition of 5 to 10 cc. of dilute barium chloride solution. This amount of *precipitant, although adequate for high sulphur steels, utterly fails* when the sulphur is very low as in the above steels, except indeed the liquid after the addition of the precipitant be evaporated to near dryness ; but since the appearance of the third edition of Blair's "Chemical Analysis of Iron," containing the recommendation to precipitate with 10 cc. of *saturated* barium chloride solution, it is extremely unlikely that such results as the foregoing have occurred.

But there is another source of error in the case of irons and low carbon steels which dissolve readily in concentrated nitric acid, *well worth noting, but not spoken of in the text-books ; this* source of error is the escape sometimes of the sulphur during solution in strong nitric acid. The following results illustrate how great the error may be from this cause :

	By aqua regia method.	
No.	As usual. Per cent.	Very slow solution. Per cent.
Iron 2456	0.006	0.012
" 2458	0.006 0.010	0.009
" 1	0.018	0.031
" 2	0.017	0.030
" 3	0.010	0.017
" 4	0.019	0.019
" 2459	0.006	0.015

For the results in the second column, solution was made very slowly by adding the acid very gradually, and while heating removing from the source of heat at the first appearance of red fumes, replacing after an interval, again removing at appearance of fumes, and so on, at no time allowing decided action.

In evolution methods a very important source of error is the escape of a part of the sulphur in combination with carbon.

This is a fact very well known, but almost universally ignored. In the following table of results the evolution method used was the cadmium chloride volumetric. The results of the last column were obtained in the laboratory of a large steel works. The drillings, however, were not the same as those the writer worked on, but were obtained from the same or nearly the same spot of the iron, and the results, although not strictly comparable with the writer's, nevertheless serve to show in a general way that the evolution method as carried out by the writer is not attended with any unusual source of error leading to low results, and that the error in question is a usual and common one.

In my determinations, after complete solution, the liquid was boiled till the cadmium chloride solution (in a Troilius bulb) was brought to a boil, then the flame lowered and after an interval of gentle boiling the hard boiling repeated as before.[1]

No.	By aqua regia method, slow solution. Per cent.	By evolution method. Per cent.	Another chemist's results. Per cent.
Iron 2458	0.009	0.010	....
" 1	0.031	0.019	0.013
" 2	0.030	0.018	0.012
" 3	0.017	0.009	0.012
" 4	0.018 0.019	0.020	0.014
" 5	0.022	0.023	0.026
" 6	0.018	0.013	0.014
" 7	0.019	0.014	0.014
" 8	0.020	0.016	0.015
" 9	....	0.014	0.013
" 10	0.021	0.012 0.016	0.015
" 11	0.019	0.016	0.013
" 12	0.027 0.025	0.014	0.014
Steel 2711	0.034	0.022	....
" A	0.018	0.018, (by another chemist).	
" B	0.020	0.020, " " "	

Steels A and B are crucible steels containing about 0.02 per

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[1] At one time the writer suspected that the low results by the evolution method were due simply to insufficient boiling, and as boiling in the way described above brought higher results and results agreeing fairly well with the results by the aqua regia method this suspicion was apparently confirmed, but the rubber tube in use at that time was the white, or vulcanized kind, and it was later found that the steam carried over sulphur from the rubber tubing, apparently as hydrogen sulphide, for in a blank test a considerable yellow precipitate was seen to form.

cent. sulphur by the aqua regia method. Five different samples of this kind of steel tested by a commercial chemist, using the evolution method, gave about 0.013 per cent. sulphur, which is what the writer also obtains in these steels by that method. At these works the malleable iron used for making crucible steel is bought under a guarantee not to exceed 0.016 per cent. in sulphur. An accurate method of determination is plainly to be desired.

From the above table it seems that sometimes the evolution method is accurate and sometimes not; it is impossible, therefore, to find a correction that will be a true one in all cases and the practice common in western Pennsylvania of standardizing the iodine solution against a standard steel of the same kind as those to be worked on must also fail at times, although it is perhaps not unlikely that the error is more regular and constant with steels than with irons. The best that can be done seems to be to note the greatest error in a series of tests and use one-half this error as a correction. According to this plan the writer, when using this method, increases his results one-fourth ; thus, for instance, 0.2 per cent. is called 0.025 per cent., and 0.012 per cent. is made 0.015 per cent. This, of course, is far from satisfactory, but seems to be the best that can be done with the method.

A difficulty in the aqua regia method is the contamination of the barium sulphate with iron oxide when the precipitation is made in solution not containing much free acid. Professor J. O. Arnold (steel works analysis) meets this difficulty by making the precipitation in the cold, but a precipitation made by the writer in this way gave a very low result, showing that precipitation in this manner cannot always be relied on as complete. Precipitating as directed by Blair, but with 5 cc. only of strong hydrochloric acid present in the liquid while preventing ferric oxide contamination, brought results 0.004 to 0.008 per cent. (generally the latter) too low, but it was found by many experiments that with this amount of acid (5 cc.) present, and with one-half hour's boiling (and standing over night), the precipitation is at least as nearly complete as by the Blair procedure and no ferric oxide contamination ever occurs, although in both methods the precipitation is rarely absolutely complete as may be found by evaporating the filtrate to first appearance of a scum, taking up with a little hydrochloric acid and water and filtering, carrying the blank, or dummy, test to the same length. Sixty-two tests (5 cc. free acid, one-half hour's boiling) showed as follows :

Number of tests in which precipitation was complete	9
" " " " " 0.001 to 0.002 per cent. was found in filtrate	34
" " " " " 0.003 to 0.004 " " " " "	11
" " " " " 0.005 to 0.008 " " " " "	8

In these losses are included also the barium sulphate dissolved by the hydrochloric acid wash used to free the precipitate from iron.

In these tests the sulphur percentage ranged from 0.015 to 0.09 per cent. The amount of sulphur unprecipitated does not depend upon the total amount—may be little in high sulphur steels and *vice versa*. So it is advisable in all cases to make a plus correction in the result of at least 0.002 per cent.

In Blair's "Chemical Analysis of Iron" the warning is given that the use of aqua regia in dissolving the drillings seems to result in loss of sulphur. Nevertheless it is necessary to use some little hydrochloric acid in the case of high carbon steels toward the end to effect complete solution. The following results obtained in the regular course of work were suspected of being low and the determinations were repeated, using the hydrochloric acid more sparingly :

No.	First determination. Percentage of sulphur.	Repeated, using HCl more sparingly. Percentage of sulphur.
609	0.005	0.013
611	0.004	0.011
814	0.014	0.020

LABORATORY OF HENRY DISSTON & SONS' STEEL WORKS,
PHILADELPHIA, PA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 55.]

ALLOYS MADE IN THE ELECTRIC FURNACE.

BY LEWIS P. HAMILTON AND EDGAR F. SMITH.

Received January 14, 1901.

DURING the past year various alloys were made by us. We desire here to give a sketch of the furnace in which they were produced, and also to briefly describe the products, as they possess interest and perhaps value.