VOL. XXI. [JULY, 1899]. NO. 7.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

CARBON COMBUSTIONS IN A PLATINUM CRUCIBLE.

BY P. W. SHIMER.

Received February 14, 1899.

THE determination of carbon by combustion in oxygen necessitates the use of a costly and bulky combustion furnace, a porcelain or platinum tube, and a supply of pure oxygen. The gas consumption is large and the heat generated is ridiculously out of proportion to the small amount of carbon to be burned. Even with this wasteful use of gas, the temperature attained, under the conditions of gas pressure existing in some laboratories, is not always high enough to ensure the complete combustion of graphite in pig iron.

In the apparatus devised by the writer, it is proposed to use a platinum crucible, with a water-cooled stopper, in place of the porcelain or platinum tube; an ordinary small blast-lamp and Bunsen burner in place of the combustion furnace; and air instead of oxygen.

The crucible is a platinum fusion crucible of the usual shape, about $1\frac{7}{16}$ inches in diameter and $1\frac{9}{16}$ inches high. In order to stiffen the top of the crucible, a ring made of ordinary sheet copper about $\frac{3}{16}$ inch wide, brazed at the ends, is fitted closely around the extreme top of the crucible. This ring is made of sheet metal so as to give the crucible the necessary support against stretching, without, at the same time, making it too rigid.

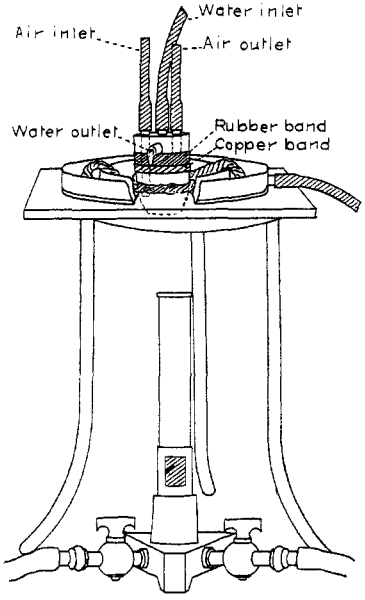

Fig. 1.

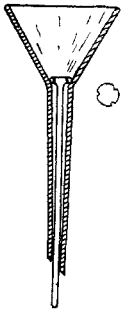

Fig. 2.

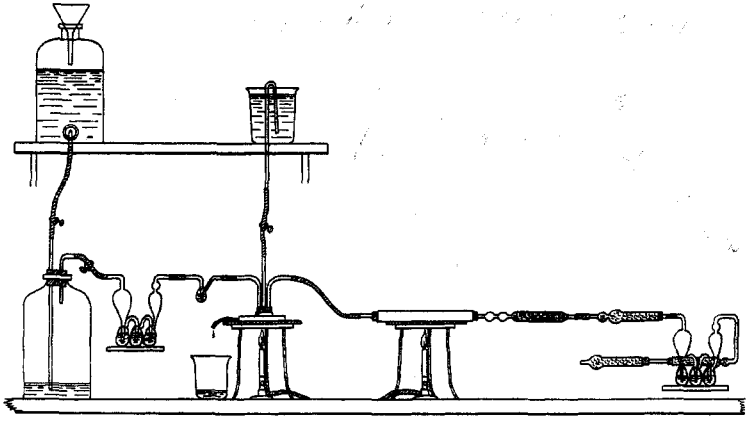

Fig. 3.

The essential part of the apparatus is the water-cooled stopper for closing the crucible. The construction of this stopper will be readily understood from the sketch. The stopper is made of sheet copper, the joints being brazed. It is, of course, essential that it should be as near perfectly circular as possible, with no indentations or imperfections in the brazing. The sides of the stopper should not flare more than the sides of the crucible at the top. Too much flare has a tendency to cause the stopper to be forced out of the crucible when under pressure.

The stopper is made somewhat smaller than the crucible opening, in order to allow space for a rubber band. This band is of pure black rubber such as can readily be obtained at most stationers. It is one-fourth to one-half inch wide and of such a length that it will stretch tightly around the lower part of the stopper. With a very little experience in putting the rubber-banded stopper into the crucible, it may be made perfectly tight with a greater degree of certainty than can the common rubber stoppers used in a porcelain combustion tube.

When the lower part of the crucible comes to a bright red heat in the course of a combustion, there is no risk whatever of burning or softening the rubber, for the band is cooled by the water passing through the stopper and by wet wick wrapped twice or more around the upper part of the crucible, the ends of the wick drawing their water from a circular copper trough kept full by the overflow from the stopper. In order to avoid any risk of softening the lower edge of the band by the heat radiating from the bottom of the crucible, the latter is always one-third to one-half full of ignited asbestos. I have used a single rubber band for as many as twenty combustions, and then discarded it only because it was becoming hard, making it more difficult to make the crucible tight.

In the train for the combustion of carbon in iron and steel, shown in the illustration, we have the following parts, beginning at the left:

1. Two aspirator bottles, the upper filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.

2. Potassium hydroxide bulbs containing potassium hydroxide of 1.27 specific gravity.

3. A little guard bottle to retain any drops of potassium hydroxide that may be forced over from the Geissler bulbs.

4. The combustion crucible connected with its reservoir of *distilled* water for supplying the stopper; the circular trough to catch the overflow and serve as a source of water for the wet wick; the piece of stout asbestos board perforated to support the crucible at a point about half way through. Under the crucible we have the blast-lamp.

5. Next to the crucible is the cupric oxide tube, a short brass or porcelain tube, ten to twelve inches long, of small diameter. In some recent experiments, a small brass tube three-eighths inch in diameter and ten inches long, filled in its middle portion with cupric oxide, was tried in place of the porcelain tube and was found to be quite satisfactory. The brass tube is filed down at the ends and the rubber tubing is stretched over them. Although a porcelain tube is shown in the sketch, I am now using a brass tube altogether. The cupric oxide tube is supported across the top of a tripod, with a single good Bunsen burner below, to heat to a red heat one and one-half to two inches of the cupric oxide. A piece of stout asbestos board is laid across the top of the tripod to retain the heat.

6. Next to the cupric oxide tube is a glass tube filled with glass beads, wet with water and kept quite cold externally by wet wick, to retain chlorine and hydrochloric acid. The wick is wrapped about the tube, the free ends hanging in a beaker of distilled water, not shown in sketch.

7. A large calcium chloride tube.

8. The potassium hydroxide bulbs with calcium chloride tube attached.

9. A guard tube of calcium chloride.

In the preliminary experiments some trouble was experienced in getting satisfactory constant weights on the potassium hydroxide bulbs. There was a constant increase in weight. After excluding all the sources of error that at first suggested themselves, there still remained an increase in weight of from 0.0007 to 0.0018 gram. In these early experiments air was *drawn* through the apparatus. It now occurred to me that possibly the permeability of platinum at a red heat was the cause of the trouble. Air was then forced through the apparatus, with the

result that the constant weights very rarely differed more than 0.0005 gram.

It might be supposed, if platinum is permeable at a red heat, that there would be loss of carbon when pressure is used. When, however, we compare the comparatively small amount of carbon drawn into the crucible when immersed in the flame, with the large total amount of carbon burned in the flame, and then imagine a like proportion of the small weight of carbon in the crucible lost by permeation, we may conclude that the loss is inappreciable. At all events the carbon results obtained in this way agree closely with standard results obtained by combustion in a porcelain tube in oxygen. Besides, if permeability of platinum is a serious matter in carbon determinations, it is strange that the users of platinum combustion tubes have not discovered it.

In the course of these constant weight experiments, it may be interesting to note in passing, the now well-known difficulty of getting closely agreeing constant weights in stormy weather was again noticed. Another source of error in getting constant weights was noted when, on one occasion, the hydrant water used in the aspirator bottles had become somewhat stagnant. There were enough gaseous products of decomposition, or of animalcular life processes, to cause increase in weight of the potassium hydroxide bulbs, which ceased as soon as distilled water was used in the aspirator bottles. These gases passed through the first potassium hydroxide bulbs and were burned to carbon dioxide in the crucible and cupric oxide tube and were then, of course, absorbed by the weighed potassium hydroxide bulbs.

The method of solution of steel for carbon determination is the standard one by use of acidified solution of double chloride of copper and potassium. The carbon is filtered upon asbestos in the following manner: A glass rod about one inch longer than the stem of the funnel (an ordinary funnel, two and one-half inches in diameter) and small enough in diameter to pass easily through the stem, is flattened out at one end and notched at two or three places by pressing the red hot glass against the sharp corner of a file. The sketch shows the flattened and notched end of the rod; also the rod in position in the stem of the funnel.

In preparing the filter, very short fibered ignited asbestos is used, with fibers not longer than one-sixteenth inch. This is well stirred up with distilled water so as to have it well in suspension in a rather large bulk of water. A small piece of dry asbestos about the size of a pea is placed in the bottom of the funnel upon the end of the glass rod. This is to prevent the finely divided and suspended asbestos from packing into the passage, thus impeding filtration. The suction is now turned on and a little of the suspended asbestos is poured on. When this has been deposited as a fine horizontal felt, pour on more asbestos. If the asbestos fibers are short enough, a perfectly tight filter may be made with not more than one-fourth inch of asbestos. A small bulk of filter greatly facilitates subsequent transference and combustion. When dry, the carbon may usually be picked off in a thin shell by means of a pair of forceps. It is easily transferred to the empty crucible, *with the carbon side down*. It is well to have a circular piece of thin platinum foil in the bottom of the crucible. The small amount of carbon remaining in the funnel is removed by use of a little ignited asbestos. It is necessary to be careful to keep all the carbon within about one-fourth inch from the bottom of the crucible, which is not at all difficult to do. If a part of the carbon were to be one-half to three-fourths inch from the bottom, it might escape complete combustion. Graphitic carbon from pig iron is easily burned in air at the white heat attainable by the blast-lamp. After the carbon is all transferred, a little ignited asbestos is filled in on top of it.

Another way is to add a little finely divided, ignited asbestos to the solution, and to filter the carbon on a Gooch crucible. The Gooch, without its cap, is then placed on the bottom of the combustion crucible. This method has the advantage of rapid filtration, quick transference, and avoidance of contact of the carbon and traces of copper oxide with the bottom of the combustion crucible. A Gooch crucible may be made out of an old ignition crucible.

There is no reason why oxygen should not be used successfully, but, when air does the work effectually, it seems unnecessary to use oxygen. An advantage of air is that the bulbs are weighed filled with air before and after the combustion, and

there is no need to replace oxygen with air as in the oxygen method.

When getting constant weight, proceed as follows: Fill the crucible one-third full of ignited asbestos and close it, first wetting the rubber band. Saturate the wick with alcohol; it is difficult to wet it with water. Wrap a long piece of the wick twice or more *closely* around the crucible as it rests in its place in the asbestos board, and allow the ends of the wick to lie in the copper trough as shown in the sketch. When a brass cupric oxide tube is used, a little wet wick wrapped several times about each end inside of the rubber connections and hanging in beakers of water, will avoid all risk of burning. The moisture tube is disconnected and filled with cold distilled water and the excess is allowed to drain out by holding the tube in a vertical position. It is then connected as shown in the sketch. Open the clamp and allow water to run out of the stopper. Now put the Bunsen flame under the crucible and the middle of the cupric oxide tube, covering the latter with a piece of asbestos board. Open the Hofmann clamp between the upper and lower aspirator bottles and leave it fully open. Open the Hofmann clamp between the lower aspirator bottle and the potassium hydroxide bulb and regulate the passage of air by this clamp alone. Let air bubble through the apparatus, rather more rapidly than in oxygen combustion, for twenty minutes. Detach and weigh with the usual precautions. A second weight nearly always agrees well with the first. My constant weights with this apparatus have deen steadily better than I have ever been able to get with the combustion furnace and oxygen, which may be attributed both to the use of air all through and to the absence of the disturbing influence of the hot furnace near the bulbs to be weighed, and the moisture-laden air resulting from the burning of large volumes of gas. When the constant weight is obtained, the carbon is transferred to the crucible as described and the combustion is begun, after, of course, testing the apparatus for tightness. Before putting the stopper into the crucible it is best to wet the rubber band with the wet finger. This prevents friction and ensures a tight crucible. In putting in the stopper do not brace the thumb against the overflow tube, for there is great risk of bending the stopper at the base of the over-

flow. Be sure that water is running from the stopper and that the cupric oxide tube is red hot for from one and one-half to two inches, then turn on the air at the speed of about three bubbles per second and bring a small blast-lamp flame immediately under the crucible so as to heat the bottom to a bright red heat, extending at least one-fourth inch from the bottom. A large flame is to be avoided. The bottom of the crucible should be flat or, better, slightly convex—*never concave*. Combustion begins immediately, and in one or two minutes carbon dioxide begins to be absorbed by the potassium hydroxide bulbs. Combustion is complete in twenty-five minutes or less. In removing the asbestos from the crucible there is often, when copper solution has been used for dissolving the sample, a black residue remaining where the carbon was, which may mislead the inexperienced, but it is oxide of copper, as is easily proved by its solubility in strong hydrochloric acid.

When the carbon, after filtration, is well washed both with hydrochloric acid and hot water, there is very little chlorine or hydrochloric acid to fear, and the moisture tube effectually stops it. After every five or six combustions, it is only necessary to rinse out the tube with distilled water and connect it again. This moisture tube has been in use in my laboratory for several years, and it has proved itself a simple and efficient means of retaining chlorine and hydrochloric acid. The tube was made for me by Greiner; it is six inches long and three-fourths inch in diameter. The two bulbs are empty; the tube itself is filled with glass beads of about one-eighth inch in diameter. The tube retains about two and a half cc. water when drained. In some experiments an acid solution of silver sulphate was used in place of water, but, under the conditions, it was not more effective than water.

It may be interesting to note here that in some experiments made to determine how near the carbon could be determined by use of the crucible without the cupric oxide tube, it was found, as was of course to be expected, that only about ninety per cent. of the carbon was oxidized to carbon dioxide and determined. Another experiment in which asbestos coated with cupric oxide was placed on top of the carbon in the crucible, without the cupric

oxide tube, gave much better results, but still slightly below the correct figures.

The following are a few carbon determinations:

	By combustion in a porcelain tube in oxygen.	By combustion in air in crucible.		
Steel A	1.035	1.034	1.035	1.039
" B	1.040		1.046	
" C	1.032		1.029	
" D	0.466		0.466	

DUPLICATE RESULTS BY COMBUSTION IN AIR IN CRUCIBLE.

Graphite in pig iron	3.327	3.334
Soft steel E	0.026	0.026
" " F	0.023	0.023
Steel G	0.188	0.187
" H	0.580	0.582

By the kindness of Mr. C. A. Buck, chemist of the Bethlehem Iron Co., I am able to give the following series of carbon results obtained by him while testing the reliability of the combustion apparatus preparatory to using it regularly in the laboratory of the Bethlehem Iron Co. For steels Mr. Buck uses fifteen minutes' combustion and five minutes' aspiration. For pig irons he uses twenty-five minutes' combustion. The results are as follows, on standard samples:

	Combustions in platinum tube.	Combustions in crucible.	Average.
Steel No. 1	1.060	1.059	
		1.058	
		1.064	
		1.066	
		1.060	
		1.063	
		1.063	
			1.062
Steel No. 2	0.490	0.491	
		0.496	
		0.488	
		0.493	
		0.490	
		0.487	
		0.488	
			0.490

	Combustions in platinum tube.	Combustions in crucible.	Average.
Steel No. 3.....	0.183	0.178	
		0.184	
		0.189	
		0.179	
		0.180	
		———	0.182
Steel No. 4.....	1.020	1.020	
		1.020	
		1.025	
		———	1.022
Steel No. 5.....	0.700	0.696	
		0.699	
		———	0.698
Pig iron No. 1—Total carbon..	3.670		3.690
Pig iron No. 2 " "	3.638	3.600	
		3.620	
		3.646	
		3.620	
		———	3.622

The crucible may also be used in the determination of carbonic acid and combined water in ores, limestone, etc. For these determinations the apparatus is arranged in the following order: The air passes first through the potassium hydroxide bulbs, then through a calcium chloride tube, then through the crucible containing the dried sample, preferably contained in a small basket of platinum foil fitting closely into the bottom of the crucible. Next to the crucible is the weighed calcium chloride tube and following this the potassium hydroxide bulbs and guard tube of calcium chloride. In determining water, it is necessary to heat the water in the beaker supplying the stopper in order to prevent condensation of moisture on it. Constant weights obtained on the calcium chloride tube with the stopper supplied with hot water agree within 0.0001 to 0.0003 gram, while, with cold water in the stopper, the increase of weight was sometimes as high as 0.0040 gram. The water condensed on the stopper would, to an appreciable extent, be drawn down under the rubber band.

In determining carbonic acid in limestone, one gram of the finely ground sample is placed in the bottom of the crucible and on top of this is placed a layer of ignited asbestos. The ignition

is maintained for a half hour. In determining water alone, there is, after the crucible, only the weighed calcium chloride tube and the guard tube of calcium chloride. The following are some results on carbon dioxide and water.

	Carbon dioxide. I.	II.	Water.
In zinc ore A	7.80–7.94		0.60
" " " B	1.35		1.12
" " " C	7.68		1.22
" " " D	1.23–1.21		0.76
" " " E	2.76		0.71
" " " F	2.58		0.55

Mr. J. W. Louder obtained the following results in determining carbon dioxide and water:

	Carbon dioxide. I.	II.	III.
In limestone A	45.80	45.65	45.62
" " B	44.29	44.38	....
	Water. I.	II.	III.
In selenite	20.13	20.12	20.23

The crucible has also been used in determining iron in iron ore by reduction in hydrogen at a red heat, solution of the reduced iron in sulphuric acid and titration with permanganate solution. In the arrangement of the apparatus for this purpose, the hydrogen is passed from the evolution flask through a wash-bottle containing strong sulphuric acid. Then through the crucible containing one-half gram of the dry ore weighed out into a small basket of platinum foil fitting the bottom of the crucible.

The ore should be roasted in air in the open crucible for about five minutes to destroy any carbonaceous matter present. It is allowed to cool and then the stopper is inserted and hydrogen is passed through the apparatus. When all air has been expelled, the crucible is heated to a red heat for one-half hour, allowed to cool perfectly in the hydrogen current, then dissolved in sulphuric acid and titrated. This method, while accurate for ores containing no iron in the insoluble residue, has no advantage over some of the more rapid methods. An Alabama hematite containing 48.36 per cent. total iron (48.24 per cent. soluble in hydrochloric acid, and 0.12 per cent. insoluble in hydrochloric

acid) gave, by reduction in hydrogen, 48.26 per cent. iron, showing complete reduction of all the iron but the small amount present in a combination insoluble in hydrochloric acid. This method is not recommended for general use, but is given merely as an illustration of the widely various uses to which the crucible may be put.

It is, however, not adapted for those organic combustions in which condensible decomposition products are formed. These condense in the cooler upper part of the crucible where they are beyond reach of the temperature necessary to burn them. Probably by mixing such organic compounds with suitable oxidizing material, such combustions might be successfully made, but this is a field that has not yet been investigated

My last combustion apparatus was made for me by the Baker and Adamson Chemical Co., of Easton, Pa., who also furnished me with a reliable quality of pure rubber bands.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 34.]

THE INFLUENCE OF TEMPERATURE ON THE SPECIFIC ROTATION OF SUCROSE AND METHOD OF CORRECTING READINGS OF COMPENSATING POLARISCOPES THEREFOR.[1]

BY HARVEY W. WILEY.

Received March 9, 1899.

THE influence of temperature on the specific rotation of sucrose has been mentioned by several authors. A partial résumé of the literature on the subject is given by von Lippmann.[2] A more detailed discussion of the subject is given by Sachs.[3] A rather full abstract of previous papers on the subject is given by Sachs, who strangely, however, fails to mention the paper of Andrews on this subject. The early writers with the exception of Dubrunfaut[4] seem to be unanimously of the opinion that the temperature exerts no notable influence on specific rotation. This is the doctrine announced by Tuchschmidt[5] and

[1] Read before the American Chemical Society and Section C, of the American Association for the Advancement of Science, at Boston Meeting, August, 1898, and before the Third International Congress of Applied Chemistry, Vienna, August, 1898.

[2] *Chemie der Zuckerarten*, Edition *1895*, page 672.

[3] *Ztschr. Rübenzuckerind.*, 46, 264.

[4] *J. prakt. Chem.*, 28, 10.

[5] *Ztschr. Rübenzuckerind.*, (*1870*), 649.