ART. XXXVI.—*A method of determining the amount of Protoxyd of Iron in Silicates not soluble in the ordinary mineral acids ;* by
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THE accurate determination of the amounts of protoxyd and sesquioxycd of iron in siliceous minerals is a point of much importance in mineralogy, and when the silicate can be dissolved by the ordinary mineral acids, this determination presents no great difficulties. But it is very different with the so-called insoluble silicates. In regard to these the problem has never been satisfactorily solved; so that the exact condition of oxydation of the iron in some varieties of the most common species is not with certainty known. Many siliceous minerals which are not perfectly decomposed by the dilute mineral acids in an open vessel, are dissolved after long digestion in a sealed flask, and in a former paper the author described a simple and accurate method of determining the amount of protoxyd of iron in all silicates of this class. The method here described applies chiefly to the silicates, which cannot be thus decomposed and is based on the use of hydrofluoric acid as a mineral solvent. With a very few exceptions all silicates are dissolved after a more or less prolonged digestion in a mixture of sulphuric and hydrofluoric acids, and in this solution the amount of protoxyd of iron can be accurately determined with permanganate of potassa. It is of course essential that the solution should be made out of contact with the air and the difficulty of fulfilling this condition with hydrofluoric acid has probably been the reason why this valuable reagent has not been hitherto used in iron determinations. This difficulty however may be completely overcome

by the apparatus represented in the accompanying figure which, although it may appear complicated at first sight, is really a simple combination of parts, which are familiar in every laboratory.

To the sides of a common copper water bath are attached three tubes as is shown in the figure. The tube on the left connects with a Mariotte's flask by which the water is maintained at a constant level in the bath. The upper tube on the right connects with a carbonic acid gas generator, while the lower tube (connected with the sink by a rubber hose), serves simply as an overflow for the water. On the cover of the water-bath close to the rim is a depressed circular groove, which receives the lip of an inverted glass tunnel. When the apparatus is in

use this groove is kept full of water by the spray from the boiling liquid and thus forms a perfect water joint; but in order to secure this result the bath must be kept nearly full of water and holes for the ready escape of the steam and spray should be provided in the copper rings, which cover the bath and adapt it for vessels of various sizes. It is evident that, by this simple modification of the ordinary water-bath, we can keep our assay surrounded by an atmosphere of steam or of carbonic acid, as may be desirable, during the whole process of digestion, and that too for an indefinite period. Moreover while watching the process through the glass we can either pour in fresh quantities of the solvent, or we can stir up the material, in the vessel within, introducing a tube-tunnel or stirrer through the spout of the covering tunnel.

After the above description the method of making the iron assay will be readily understood. A small amount of the finely

pulverized mineral (from one-half a gram to a gram) is weighed out in a large platinum crucible. Upon this we pour a mixture of dilute sulphuric acid (sp. gr. 1.5) with as little hydrofluoric acid as experience may show is required to dissolve* the mineral stirring up the material with a platinum spatula. The crucible is next transferred to the water bath, the covering tunnel put in place, water poured into the groove, the interior filled with carbonic acid from the generator and the gas lamp lighted. As soon as the water boils, the connection with the generator is closed, and if the water level has been properly adjusted, the apparatus will take care of itself, the groove will be kept full of water and the interior of the tunnel full of steam. If the materials cake on the bottom of the crucible,—as is not unfrequently the case when a large amount of insoluble sulphate is formed,—the lamp may be removed, the apparatus again filled with carbonic acid, and the contents of the crucible stirred up as above described. A stout platinum wire about two inches long, cemented before the blow-pipe to the end of a glass tube, makes an excellent stirring rod, and after using it any adhering material can easily be washed back into the crucible by directing the jet from the wash bottle down the throat of the covering tunnel. The lamp may then be replaced, the current of carbonic acid interrupted and the process of digestion continued. When the decomposition is complete the current of carbonic acid gas is reestablished, the lamp extinguished and the air tube of the Mariotte's flask raised until its lower end is above the level of the overflow. A slow current of water is thus caused to flow through the bath, which soon cools down the whole apparatus. The crucible may now be removed, its contents washed into a beaker glass and the solution diluted with pure water until the volume is about 500 c.m.³, when the amount of protoxyd of iron present can be determined with a solution of permanganate of potassa in the usual way. The total amount of iron present being subsequently determined, the relative proportion of the two oxyds is of course well known. In order to show the accuracy of the method and also to prove that the presence of hydrofluoric acid does not exert any appreciable influence on the permanganate solution we subjoin the following results.

The strength of the solution of permanganate was tested with the double sulphate of ammonia and iron. In each case 1.4 grams of the salt were accurately weighed out and dissolved in about 500 c.m.³ of water. To the first two portions sulphuric acid was alone added while to the last two there was also added a very large amount of hydrofluoric acid, four or five times as

* If the mineral contains lead, baryta, strontia or even lime in any considerable quantity, complete solution cannot of course be obtained, but this is unimportant so long as the mineral is wholly decomposed.

much as would be required in any mineral analysis. The results were

No. 1,	1.4	grams	iron	salt	required	26.35	c. m. ³	permanganate.
No. 2,	"	"	"	"	"	26.35	"	"
No. 3,	"	"	"	"	"	26.4	"	"
No. 4,	"	"	"	"	"	26.45	"	"

From a specimen of very dark green actinolite treated as above described we obtained in three determinations the following results.

No. 1,	0.6913	grams	of	mineral	required	14.1	c. m. ³	permanganate.
No. 2,	0.6640	"	"	"	"	13.6	"	"
No. 3,	0.8910	"	"	"	"	18.2	"	"

The per centage composition deduced from this is

	Per cent of FeO.
No. 1,	19.86.
No. 2,	19.95.
No. 3,	19.89.

In order to test still further the efficiency of our apparatus we have several times dissolved 2 decigrams of iron in dilute sulphuric acid and heated the solution in the bath for more than twelve hours without its undergoing the slightest oxydation.

It is of course essential in this process that both the sulphuric and hydrofluoric acids should be perfectly pure and wholly free from any oxydizing or reducing agents. There is no difficulty in obtaining from the manufacturers pure sulphuric acid, but unfortunately the commercial hydrofluoric acid is apt to be very impure and must be carefully purified by repeated distillation before it is used in this process. The apparatus here described will also be found very useful in the ordinary iron assays and is also applicable in a large number of analytical processes, where it is necessary that the assay should not be exposed to the air. Of course in such cases a glass beaker would take the place of the platinum crucible, as is shown in the figure. Lastly, this method of heating in an atmosphere of steam will be found very convenient in the many cases where it is desirable to prevent the evaporation of water during the process. The presence of the steam moreover, prevents to a great degree the escape of the volatile acids; so that in the process above described, the glass covering tunnel is not perceptibly corroded unless the hydrofluoric acid used is very strong.

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