NOTES.

Titration of Ferrous Salts in the Presence of Hydrochloric and Phosphoric Acids.—Referring to a recent article by Elwyn Waller concerning the use of calcium phosphate in solutions containing hydrofluoric acid, when the solution is to be titrated by potassium permanganate, to obviate the bad effect of the hydrofluoric acid on the permanganate, it seems to me that the beneficial agent in this reaction is really the phosphoric acid.

I wish to state that the use of phosphoric acid alone in iron solutions to be titrated by potassium permanganate was first proposed by me about two years ago; my experiments and conclusions were published in the *Western Chemist and Metallurgist,* for Nov., 1907.

In trying to devise an improved method for the determination of iron in bone-black (which is nearly pure calcium phosphate), I found that the solution acidulated with hydrochloric acid could be titrated directly by permanganate, with great accuracy, the results checking with those made by the standard bichromate method, to hundredths of a per cent.

As the hydrochloric acid present seemed to have no effect on the permanganate, I reasoned that this must be due to the action of the phosphoric acid.

The method as applied to bone-black was as follows: The hydrochloric acid solution of the bone-black, after filtering off the carbon, was nearly neutralized by sodium carbonate to faint opalescence, then acidulated with 1 or 2 cc. of concentrated hydrochloric acid, the carbon dioxide expelled, the solution reduced by addition of sodium sulphite, the sulphur dioxide expelled, the solution diluted with cold water to about 300 cc., and titrated with potassium permanganate.

After securing such favorable results on bone-black, I was impelled to try the method in the titration of iron in iron ores. I found it worked perfectly and gave extremely accurate results, provided one or two precautions were observed, namely, the use of a minimum amount of hydrochloric acid, not over five to ten cubic centimeters of concentrated acid, at the most, titration in a cold solution of about 300 cc. volume, and the avoidance of stannous chloride in reducing the iron.

The iron may be advantageously reduced by sodium sulphite, by aluminium, by zinc, or by test-lead. If test-lead be used, the reduction may be satisfactorily accomplished in a strongly acid solution, or in one that has been almost neutralized by sodium carbonate; and where we cannot avoid the presence of much hydrochloric acid, this reduction by test-lead in a nearly neutral solution would appear to be the best; or we can use zinc dust (powder), which also acts most rapidly in a nearly neutral solution.

It must not be thought that this improvement is simply a modification of the old Zimmerman-Reinhardt method. In that method the manganese sulphate takes up hydrochloric acid, becoming manganese chloride, and the phosphoric acid present was supposed simply to decolorize the ferric iron and keep the solution colorless. But we see now that the phosphoric acid really plays a double rôle, and the addition of manganese sulphate and sulphuric acid is not at all necessary.

As the titration of iron solutions by potassium permanganate is much the preferable method in technical work, owing not only to its rapidity and ease of execution, but also to the sharpness of the end reaction, it seems to me that any suggestion that will tend to improve the method and make it more general of application cannot fail to be of great value to technical chemists generally. GEORGE J. HOUGH.

The Action of Coke on Solutions of Ferric Chloride.—In a previous communication[1] the author gave some data showing the extent to which iron is removed from a solution of ferric chloride by filtration through coke.

The opinion was then expressed that this action was largely due to sulphur compounds which had not been wholly removed from the coke. A new series of experiments has been made to test this view, such precautions to eliminate sulphides from the coke being taken as the author's slender laboratory equipment would permit, and the results have confirmed the author in his opinion. The conclusion is, in brief, that no iron was taken up by coke so treated, from an approximately decinormal solution of ferric chloride under a variety of conditions, though a part of the salt was reduced to the ferrous condition. Coke similarly prepared did not abstract any copper from an approximately decinormal solution of cupric chloride. This last is in accord with the statement of W. O. de Coninck,[2] who, however, originally stated that the iron was abstracted from ferric chloride solution.

The following are the details of the new experiments:

Preparation of Coke.—Ordinary coke was ground and passed through a sieve of 100 meshes to the inch. It was then treated with hydrochloric acid, and after that with a mixture of concentrated hydrochloric and nitric acids. After standing a few days the acids were decanted off and the coke washed repeatedly with water, dried in the air and on the steam bath. Any higher temperature was avoided lest by local superheating residual sulphates should be converted into sulphides. The coke so treated, when heated with hydrochloric acid, gave no fumes capable of darkening lead test-paper.

Ferric Chloride Solution.—To a concentrated and acid solution of ferric chloride, sodium carbonate was added in such quantity that, though

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[1] THIS JOURNAL, 31, 461.

[2] *Compt. rend.*, 130, 1551.