

fact that (exclusive of the mass) the properties of a solution are never found to be quite equal to the sum of the properties of solvent and solute. Moreover, facts known at present concerning both dilute and concentrated solutions are entirely compatible with it, and it will no doubt prove a most valuable aid in further research.

LABORATORY OF PHYSICAL CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WIS.

THE VOLUMETRIC DETERMINATION OF MANGANESE IN IRON AND STEEL.

BY HARRY E. WALTERS.

Received January 26, 1903.

In a recent number of this Journal, **24**, 1206 (1902), there appeared an article by Stehman entitled "The Determination of Manganese in Iron and Steel" in which the author stated that in attempting to replace lead peroxide with ammonium persulphate and titrating with sodium arsenite, the silver salt, of course, caused trouble. If, however, the silver salt is thrown out of solution before the titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

With the exception of the titration, the method is the same as that proposed by me in September, 1901.¹ While preparing that method the writer also tried to make a titration method but without success, as the hot solutions were titrated and the reaction between the excess of persulphate and the silver nitrate caused the results to be high and irregular.

Since the article by Stehman appeared, I have doubted the necessity of precipitating the silver as chloride, if the solution be cooled before the titration is begun. In order to prove the correctness of this view a number of samples were taken and treated as follows: 0.2 gram of the samples and a standard steel of known manganese content were weighed off into suitable test-tubes or beakers and 10 cc. of nitric acid (sp. gr. 1.20) were added to each. The solutions were heated until the samples were dissolved and all nitrous fumes driven off. Fifteen cc. of a solution of silver nitrate equal to 0.02 gram silver nitrate (1.33 grams of the salt to

¹ This Journal, **24**, R. 12.

1 liter of water) were added to each. About 0.5 gram ammonium persulphate was added and the solutions were heated until the oxidation commenced, and then for about a half minute longer. The solutions were then cooled.

In preparing the iron samples 1 gram was dissolved in 30 cc. of nitric acid (sp. gr. 1.20) filtered into a 100 cc. calibrated flask and diluted to the mark. After thorough mixing, 20 cc. of the solution were transferred to test-tubes or beakers and a little ammonium persulphate added to destroy the combined carbon. Five cc. of a solution of silver nitrate (4 grams of the salt to 1 liter of water) and a little more persulphate were added and the procedure continued the same as for steels.

When the permanganic acid solutions were cold, they were treated as follows:

First Series.—The manganese was estimated colorimetrically.

Second Series.—The silver was precipitated as chloride and the solutions were then titrated with a sodium arsenite solution until the disappearance of the pink color.

Third Series.—The solutions were titrated with sodium arsenite without precipitating the silver as chloride.

Fourth Series.—The solutions were titrated with hydrogen peroxide without precipitating the silver as chloride.

The following results were obtained:

Sample.	Colorimetric.	Arsenite titration.		Hydrogen dioxide
		Silver precipitated.	Silver not precipitated.	titration. Silver not precipitated.
Steel No. 18 ..	0.28	0.269	0.281	0.27
" " 17 ..	0.47	0.46	0.48	0.47
" " 11 ..	0.53	0.55	0.544	0.533
" " 22 ..	0.57	0.588	0.595	0.59
" " 26 ..	0.40	0.44	0.428	0.426
" " 33 ..	0.49	0.495	0.493	0.492
" " 90 ..	0.90	0.92	0.902	0.89
" " 47 ..	0.43	...	0.43	0.43
Iron S.....	0.19	...	0.21	0.19
" No. 712....	0.22	...	0.22	0.21
" " 713....	0.23	...	0.234	0.24
" " 716....	0.24	...	0.24	0.245
" " 828....	0.16	...	0.16	0.15
" " 813....	0.13	...	0.11	0.11
" " 829....	0.18	...	0.17	0.19
Steel No. 68 ..	0.73	0.72	0.74	0.74

It will be observed that the results all agree closely whether the silver was separated or not, and that hydrogen peroxide (as was to be expected) may be used as well as the sodium arsenite. The end-point in all these titrations is not as sharp as might be desired but I think it is sharper if the silver is not precipitated. If the silver is not precipitated, the titration must be done quickly, as the persulphate and silver nitrate in solution react to reproduce the color, if allowed to stand.

LABORATORY UNITED ENGINEERING AND FOUNDRY COMPANY,
LINCOLN FOUNDRY COMPANY DEPT., PITTSBURG, PA.

THE CORROSION OF IRON.

BY W. R. WHITNEY.

Received January 30, 1903.

It is my object to add to the literature on this subject, the results of some observations of the action of water or steam under various conditions upon ordinary iron, coupled with some consideration of the principles involved.

Owing to the great use made of iron and steel, and the dependence placed upon them, it is not surprising to find that a great deal has been written upon the factors influencing their length of life when used for various purposes.

Practically the only factor which limits the life of the iron is oxidation, under which are included all the chemical processes whereby the iron is corroded, eaten away, or rusted. In undergoing this change, the iron always passes through or into a state of solution, and, as we have no evidence of iron going into aqueous solution except in the form of ions (probably electrically charged atoms), we have really to consider the effects of conditions upon the potential-difference between iron and its surroundings. The whole subject of corrosion of iron is therefore an electrochemical one, and the rate of corrosion is simply a function of electromotive force and resistance of circuit. If now we apply Nernst's conception of the source of electromotive force between a metal and a solution, we must conclude from the measured potential-difference that iron in contact with an aqueous solution tends to dissolve, ionize, or oxidize with a force expressed as equivalent to about 10,000 atmospheres' pressure at ordinary temperature.

In other words, iron should tend to dissolve in any aqueous