

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED
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THE THERMOCHEMISTRY OF IRON AND STEEL.

[A WITHDRAWAL.]

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IN 1897 I published in connection with Mr. F. Thompson an article entitled "A Preliminary Thermochemical Study of Iron and Steel."¹ In this article some of the results given were so unusual, that it was deemed desirable to continue the work along the same lines of investigation. The work was taken up again in the autumn of 1897 by Mr. W. E. Hartman. The first experiments undertaken were to verify the results reported in our first paper as having been obtained by Mr. Thompson. Mr. Hartman was unable to duplicate the results obtained by Mr. Thompson and as a result of this I published "A Correction," in this Journal.²

During the past two years my three assistants, Messrs. W. E. Hartman, Carl Sundstrom, and E. C. Champion have worked independently in an effort to explain the very unusual results reported in our first paper. Our efforts have been towards eliminating the sources of error as much as possible; to this end the calorimeter employed has been improved in many of its mechanical details, the time of solution has been reduced to usually less than four minutes. The rate of loss by radiation for each 0.1° has been determined as well as the slight gain in heat due to oxidation of cuprous chloride by dissolved air. With the most careful manipulation the difference between duplicate determinations could be kept down below 1 per cent. of the observed amount.

The first experiments undertaken were to determine the influence of the amount of free hydrochloric acid in the solution of ammonium cupric chloride employed. An interesting fact was developed at this point; it was found that if pure carbide of iron, $(CFe)_n$, isolated by electrolysis from annealed steel, was added to neutral ammonium copper chloride there was little or no action, the thermometer in the calorimeter rising less than 0.01° C. in five minutes; if, however, the ammonium copper chloride solution

¹ This Journal, 19, 754.

² *Ibid.*, 20, 78.

contained 0.09 per cent. of free hydrochloric acid, there was marked action, and with 0.46 per cent. of free hydrochloric acid, solution of 1 gram of carbide was complete in two minutes.

Other experiments were made with increasing amounts of free hydrochloric acid up to 4 per cent., the amount used in our previous work, and although it was found that some free hydrochloric acid is necessary in order to obtain complete and rapid solution, the amount of free acid up to 4 per cent. did not appreciably influence the amount of heat evolved; practically all of the iron was dissolved by its reaction with cupric chloride and not by direct solution in hydrochloric acid. The solution finally adopted for all of the later work contained 0.84 per cent. of free hydrochloric acid.

The difficult solubility of carbide of iron in neutral ammonium cupric chloride will easily account for the results obtained by Osmond quoted in our first paper. These results go to show that if steel be quenched or cold-rolled the heat of solution is thereby markedly increased. The effect of heating and quenching steel as well as of cold-rolling is to render the carbide much more easily soluble in neutral solution than when existing in annealed metal.

The results of the experiments carried on during the past two years by Messrs. Hartman, Sundstrom, and Champion have agreed with each other within the limits of experimental error. These results all go to prove that the heat of solution of steel determined in slightly acid ammonium copper chloride is not varied at the outside more than 2 per cent. by variation in the heat or mechanical treatment of the sample nor by variations in chemical composition within the limits of ordinary steel.

In view of these later experiments it must be acknowledged that the results reported in our first paper have no foundations in fact, and I would therefore request that they be considered, if possible, as withdrawn.

I regret that results of experimentation which have not been confirmed by a second worker, should have been published from this laboratory.

ANN ARBOR, MICH., February 10, 1900.

[EDITORIAL NOTE: It would be unfair to print the above without reminding the reader that Dr. Campbell's eyesight was destroyed several years since in a laboratory accident, and in consequence he has since then been entirely dependent upon others in this respect].