In electrolytic determination of metal where they are deposited in platinum dishes, the results will be found to be much more satisfactory, if duplicate determinations are made in platinum dishes of practically the same size, and the dishes are washed, dried, cooled, and weighed under the same conditions, each dish serving as a counterpoise for the other. By using dishes in this way, variations of weight due to atmospheric changes may be reduced to a minimum and the results made more accurate than when a dish is weighed alone.

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[CONTRIBUTIONS FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

ON THE INFLUENCE OF SILICON UPON THE HEAT OF SOLUTION OF COKE CAST IRONS.

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THE principal object of the following research was to determine if any thermochemical evidence could be obtained indicating a change in the condition in which silicon exists in cast iron, this change being due to differences of the temperature at which the iron is made. It is well known that when the temperature in a blast-furnace passes a certain point, namely, that at which No. 1 foundry iron is made, the color of the cast iron produced changes somewhat as the temperature of the furnace rises. This change continues until it reaches the temperature at which silvery or glazed iron is made, when there is a very abrupt change in the appearance and properties of the iron. It was thought that the appearance peculiar to silvery iron might be due to a change of form in which the silicon exists, and that this change might be indicated thermochemically.

The cast irons used in this work, with the exception of the two ferrosilicons, were all made in the same blast-furnace from approximately the same stock. They were selected from among a large number of samples with a view to obtaining a regularly increasing per cent. of silicon as the temperature at which the iron was produced increased, this temperature being judged by the grade of the iron.

The chemical analyses upon these irons included the determinations of graphitic carbon, manganese, phosphorus, silicon, and total iron. In addition, after the samples had been dissolved in the calorimeter, the amounts of iron and phosphorus in the insoluble residue were determined. From these two latter results the amount of iron oxidized to ferrous chloride and of phosphorus oxidized to phosphoric acid could be found. All the manganese passes into solution as manganous chloride.

In the calorimetric determinations, a one-gram sample was used in all cases. The solvent was a solution of ammonium copper chloride made up in the molecular ratio,

$$(NH_4Cl)_2CuCl_2 : 50H_2O,$$

but with the addition of 0.84 per cent. of free hydrochloric acid. It was found that when a sample of pure carbide of iron, of the empirical formula CFe_3,[1] was treated with strictly neutral ammonium copper chloride solution, there was apparently no action at all, the carbide remaining unaltered. The addition of only 0.09 per cent. free hydrochloric acid induced marked action, while with 0.84 per cent. of free acid solution of one gram was complete in two minutes. Pure water acidified with 0.84 per cent. of free acid was without appreciable action upon the pure carbide of iron. Owing to the greatly increased chemical activity of a slightly acid solution, compared with that of a strictly neutral one, it was thought best to use the former, as there seemed to be no danger of direct reaction between the hydrochloric acid and the metal under treatment.

The rise of temperature of the solution in the calorimeter was determined by means of a Beckmann thermometer, graduated in hundredths of a degree, the graduations being large enough so that with the aid of a reading glass, readings could be made in thousandths of a degree, with an error not exceeding two thousandths. The rise of temperature in the calorimeter varied for the different samples between 2.780° and 3.715°.

Owing to the varying lengths of time required for solution of the different samples, corrections were made in all cases for the loss by radiation. In each calorimetric determination readings were made at the end of each minute until a fall in the thermometer indicated complete solution; and corrections were

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[1] "A Pure Carbide of Iron"—*Am. Chem. J.*, 18, 836.

made for loss according to the difference in temperature at the time of each reading. The rate of loss by radiation for varying temperatures was determined for differences of 1°, 2°, and 3° between the initial and final temperatures; and it was found that for twenty-five minutes, the rate of loss by radiation for any given difference, was constant. For a difference of 3° between the initial and final temperatures the rate of loss was 0.015° per minute. The correction that had to be applied because of this loss varied between 9.6 and 20.1 calories with the exception of one case in which the solution required twenty-two minutes, necessitating a correction of ninety-eight calories. It was also found that a second correction had to be made owing to the slow oxidation of the cuprous to cupric chloride by the air dissolved in the solution. This oxidation takes place most rapidly during the first ten minutes, after which the rate falls off as the amount of dissolved air present, diminishes. The correction due to this oxidation amounts to six-tenths of a calorie per minute for the first ten minutes, which amount falls to 0.36 calorie during the succeeding five minutes, and to 0.24 calorie at the end of fifteen minutes from the start. This correction was determined by dissolving 1.132 grams of pure copper, the chemical equivalent of one gram of pure iron, and noting the slow, continuous rise of temperature after the copper was completely in solution as cuprous chloride.

In the reduction of the results to absolute calories, since we had not access to apparatus for determining accurately the specific heat of a solution, resort was made to an indirect method for the determination of the water equivalent of our solvent. The following data were used: specific heat of glass, 0.177; specific heat of mercury, 0.033: specific heat of iron, 0.111; calories evolved by one gram of iron when dissolved in ammonium copper chloride, 719.3. This last figure was obtained from the heats of formation of ferrous, cupric, and cuprous chlorides as given in Thomsen's "Thermochemische Untersuchungen," 3, 506.

$$\mathrm{Fe} + 2\mathrm{CuCl_2} = \mathrm{FeCl_2} + 2\mathrm{CuCl},$$
$$\mathrm{Fe} + (2 \times 62710) = 99950 + (2 \times 32875),$$
$$\text{or } 40280 \div 56 = 719.3 \text{ calories.}$$

Figuring from these data, by dissolving one gram of pure iron and dividing 719.3 by the rise of temperature, correcting for loss by radiation and for gain by oxidation of cuprous chloride, the water equivalent of the solution used and containing vessel, thermometer, and stirrer could be calculated. By subtracting the water equivalent of these latter, the specific heat of the solvent was found. This gave 0.8226 as the specific heat of the solution used.

Since the cast irons, with the exception of the ferrosilicons which were nearly free from manganese, contained from 0.46 to 1.05 per cent. of manganese, a correction had to be made for the heat evolved in its solution. From the equation:[1]

$$Mn + 2CuCl_2 = MnCl_2 + 2CuCl,$$
$$Mn + (2 \times 62710) = 128000 + (2 \times 32875),$$
$$\text{or } 68330 \div 55 = 1242.3 \text{ calories for one gram.}$$

This would require a correction of 1.24 calories for each 0.001 gram of manganese.

The corrections necessitated by the presence of manganese varied between 6.3 and 15.6 calories. A similar correction was introduced on account of the presence of phosphorus. The total phosphorus in the cast irons varied between 1.120 and 1.424 per cent.; but the amount oxidized was from 0.325 to 0.656 per cent. So correction was made only for the phosphorus oxidized to phosphoric acid.

$$P_2 + 10CuCl_2 + 5H_2O + Aq. = P_2O_6Aq. + 10CuCl + 10HCl,^{[2]}$$
$$P_2 + (10 \times 62710) + (5 \times 68360) =$$
$$405500 + (10 \times 32875) + (10 \times 39315).$$
$$\text{or } 158500 \div 62 = 2556.5 \text{ calories for one gram.}$$

This would require a correction of 2.56 calories for 0.001 gram phosphorus, or from 9.5 to 18.8 calories for the various samples dissolved.

In determining the amount of heat evolved by the oxidation of the silicon present, the heat of solution of one gram of the sample was found, correction being made for the loss by radiation and gain by oxidation of cuprous chloride. The number of calories per gram of iron dissolved was calculated by dividing

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[1] Thomsen's Thermochemische Untersuchungen, 3, 506.

[2] *Ibid*, 3, 506 ; 2, 398 ; 2, 409 ; 3, 506 ; 2, 399.

this first figure by the per cent. of iron actually obtained in solution. From the figure thus derived was subtracted the amount of heat due to the manganese and the phosphorus oxidized with one gram of iron, in addition to 719.3 calories, the heat evolved by solution of one gram of pure iron. The remainder thus obtained was assumed to be the heat evolved by the oxidation of the silicon accompanying one gram of iron dissolved. From the heat due to the oxidation of the silicon accompanying one gram of iron, the number of calories for one gram of silicon was then calculated.

The calorimetric results obtained from the cast irons examined, are best shown in the subjoined table:

Grade of iron.	Per cent. of silicon.	Calories for one gram of sample.	Time in minutes required for solution.	Calories for one gram of iron dissolved.	Calories from oxidation of the silicon with one gram of iron.	Calories from oxidation of one gram of silicon.
Ferrosilicon	13.63		No action.			
Ferrosilicon	11.79	982.3	22	1163.9	444.6	3183
Silver-gray cast iron	6.16	820.4	7	968.9	215.2	2959
Silver-gray cast iron	4.69	765.6	6	900.4	150.2	2760
No. 2 soft cast iron	4.15	769.6	3	880.5	137.9	2904
No. 1 soft cast iron	3.55	765.9	4	873.1	133.6	3303
No. 1 foundry cast iron	3.13	732.4	3	835.0	91.3	2561
No. 2 foundry cast iron	2.56	720.6	5	817.9	79.5	2731
No. 3 foundry cast iron	2.05	710.9	3	797.0	59.7	2598
Gray forge cast iron	1.40	690.5	5	781.1	42.4	2677
Mottled cast iron	0.89	672.7	11	741.3	—2.9	—298
Mottled cast iron	1.33	700.8	3	868.4	28.9	1989
Mottled cast iron	2.35	730.9	3	812.1	64.8	2822

A study of the above table seems to indicate the following facts:

First: When either from a sufficiently high temperature of the blast-furnace at the time the iron is made or from the presence of a moderate amount of silicon, probably about one and four-tenths per cent., the carbon is nearly all in the graphitic or graphitic temper form; then the heat evolved by the oxidation of the silicon is proportional to the amount of silicon present.

Second: When from a low temperature in the furnace accompanied by low silicon the carbon is largely in the combined form; then the heat rendered sensible is very much diminished owing to the large amount of heat necessary to decompose the compounds of iron and carbon, or possibly compounds of iron, silicon, and carbon, or of carbon and silicon.

Third: Since from the equation:

$$Si + 4CuCl_2 + 2H_2O = SiO_2Aq + 4CuCl + 4HCl,$$

$$Si + (4 \times 62710) + (2 \times 68360) = 207400^1 + (4 \times 32875) + (4 \times 39315),$$

$$\text{or } 108600 \div 28.4 = 3824,$$

we see that the oxidation of one gram of silicon alone evolves 3824 calories, and the results obtained by dissolving cast irons give a maximum of 3303 calories, it is evident that the compound of silicon with iron must have a very considerable heat of formation. This would indicate as a minimum for the equation:

$$Si + Fe_n = SiFe_n + 14900 \text{ calories.}$$

If the mean of all the determinations, excluding the results on the two mottled irons containing high carbon, is taken, then the heat of formation would be increased to 27,700 calories.

Fourth: When the per cent. of silicon is sufficient or nearly sufficient to correspond with the empirical formula $SiFe_3$, the compound is insoluble in ammonium copper chloride. This is shown in the case of the higher silicon ferrosilicon.

These results are not in complete agreement with those obtained by F. Osmond,[2] but the differences may be ascribed either to the fact that he used samples of iron very low in all elements other than silicon, or to the fact that he used strictly neutral ammonium copper chloride instead of a slightly acid solution, which we have shown is much more active than the former.

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[1] *Compt. rend.*, 113, 475—"Recherches calorimetriques sur l'etat du silicium et de l'aluminium dans les fers fondus," par F. Osmond.

[2] *Compt. rend.*, 113, 474.