

It is probably assuming too much for one to assert, or to state as having proved, that certain bodies completely arrest digestion. This will be seen at once if we consider that these artificial processes of digestion probably differ in a great many respects from those natural processes occurring in the stomach and intestines.

An answer to the question, "Does a substance seriously arrest digestion?" is perhaps not, strictly speaking, to be given in general, because the results obtained hold good only for the conditions under which the experiments were conducted; in other words, the neutralization capacity of the products of digestion must be taken into consideration. However, if we can show that some substances by themselves entirely, or nearly so, neutralize the action of the digestive ferments, we must naturally, and justly too, I think, infer that they have a very decided unwholesome effect on some of nature's functions. For, even if we assume that as fast as one portion of the digestive fluid is neutralized more is supplied until the right proportion for normal digestion is reached, one must see what a drain these inimical substances cause the organs to be subjected to. The organs supplying the fluids must be subjected to double, triple, or perhaps even more, work than that which normally they are required to perform; and the food too remains in the stomach and intestines a much longer period of time than usual, which fact alone would prove the arresting power of these foreign bodies.

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## A PRELIMINARY THERMOCHEMICAL STUDY OF IRON AND STEEL.

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Received June 29, 1907.

**A**LTHOUGH much work has been done upon the relation between the ultimate chemical composition and the mechanical and magnetic properties of iron and steel, very little has been done in the way of studying the question from a thermochemical standpoint.

In 1875 Troost and Hautefeuille<sup>1</sup> determined the amount of

<sup>1</sup> *Compt. rend.*, 80, 964.

heat evolved by treating several samples of pure iron, steel, and cast iron, with moist mercuric chloride, and came to the conclusion that the chemical compounds of iron and carbon were endothermic, that is, formed with absorption of heat, although those of manganese and carbon were exothermic. Later, in 1885, Osmond,<sup>1</sup> working in Troost's laboratory, obtained by dissolving samples of soft, medium, and hard steel, as well as white iron in ammonium copper chloride, results that contradicted those previously obtained by Troost and Hautefeuille. Osmond does not attempt to reduce the results obtained to calories, but states them in the number of degrees that 500 cc. of a saturated solution of ammonium copper chloride would be raised by dissolving one and a half grams of the metal operated upon.

He does not state the composition of the three steels and one white iron, except the per cents. of carbon, which were 0.17, 0.54, 1.17, and 4.10, respectively.

The rise in temperature for the three steels and cast iron is given by Osmond, as follows :

Metal.	Carbon.	Annealed.	Cold rolled.	Quenched.
1	0.17	2.151	2.247	....
2	0.54	2.111	2.207	2.222
3	1.17	1.895	2.018	2.056
4	4.10	1.419	....	1.632

From the fact that as the carbon increases the heat of solution of the annealed metals decreases, Osmond concludes that the combination of iron and carbon is accompanied by evolution of heat, not as Troost previously stated, with absorption of heat.

In order to bring out more clearly the influence of cold rolling and of hard metal, Osmond tabulates the above results, using the heat of solution of the annealed metal in each case as unity. The table given is as follows :

Metal.	Annealed.	Cold rolled.	Quenched.
1	1.000	1.045	....
2	1.000	1.045	1.052
3	1.000	1.065	1.084
4	1.000	....	1.150

Osmond says : " These results are conclusive ; in every case, quenching, like cold rolling, is characterized by an augmentation in heat, which increases with the carbon content. We

<sup>1</sup> *Compt. rend.*, 100, 1228.

believe then, that the already very probable existence of two isomeric varieties of iron,  $\alpha$  and  $\beta$ , may be considered as established.

“The crystallized, at least partially crystalline,  $\alpha$ -iron is obtained by raising to full red heat, followed by slow cooling (annealing); it is transformed into  $\beta$ -iron (which the structure of quenched steel warrants us in regarding as amorphous) either by a permanent deformation at low temperature, or by rapid cooling from a red heat, but only then in the presence of carbon or of some other bodies (manganese, tungsten) exerting the same influence upon the properties of steel.”

In order to maintain the allotropic hypothesis above stated, we must assume the heat of solution of  $\alpha$ -iron to be less than that of  $\beta$ -iron, and yet although the difference in the heat of solution of the annealed and quenched specimens given increases with the increase in the per cent. of carbon, the absolute amount of heat evolved by the high carbon steel quenched, containing presumably all  $\beta$ -iron, is not so great as that of the low carbon annealed steel, presumably  $\alpha$ -iron.

It was to try to determine whether carbon alone was responsible for the variations in the heat of solution of steels subjected to different heat treatments, that we undertook the work described hereafter.

The calorimeter employed consisted of four concentric beakers, the first and second, and third and fourth being separated by felt packing, leaving a closed air space between the second and third. The beaker in which the solution was performed was supported on a light cork ring cemented to the bottom of the inner beaker of the calorimeter, and was prevented from upsetting or touching the sides of this latter by thin strips of cork cemented to the sides of the inner beaker. The cover of the inner beaker consisted of a layer of felt held between disks of vulcanized rubber. This cover fitted close inside the inner beaker of the calorimeter and was perforated for the admission of the thermometers and stirrer.

The thermometers had a range of  $10^{\circ}$  each and were graduated to fiftieths of a degree. The stirrer, which extended almost to the bottom of the beaker in which the solution was performed, consisted of a glass rod bent at its lower end so as to stir the

entire solution and provided with small pieces of rubber cemented to it in such a way that they would sweep the entire bottom of the beaker, thus stirring up particles of metal and hastening the solution. Without the use of this device it was found impossible to get complete and certain solution in a short time, while with its use the time did not usually exceed fifteen to twenty minutes.

The stirrer was actuated constantly during the work by a water motor, the belt from which passed through a small hole in the wall of the constant temperature room in which the experiments were performed. The solution of all the samples was made in a slightly acid solution of potassium copper chloride made by dissolving the following constituents.

	Grams.
CuCl <sub>2</sub> , 2H <sub>2</sub> O .....	368.24
KCl .....	325.80
HCl (41 per cent. HCl) .....	255.01
H <sub>2</sub> O .....	1995.26

The constituents were accurately weighed out in each case on a large balance having a capacity of five kilos, and sensitive with this load to five milligrams, so that all solutions used throughout the work were practically identical.

The stock solution, after making, was allowed to stand over night, and was then filtered through asbestos and kept in a constant temperature room until ready for use. The mean specific heat of this solution was calculated from the weight of the constituents, using the following specific heats: Water 1, copper 0.095, potassium 0.164, chloride 0.1221, hydrogen in hydrochloric acid 3.41.

The mean specific heat of this stock solution, using these constants, was 0.748. The water equivalent of the beaker in which the solution was effected, of the immersed portion of the stirring rod, and the thermometer bulbs, was calculated from the weight of these, using 0.177 and 0.033 as specific heats of glass and mercury respectively. Although there may be a slight absolute error in the reduction of the temperatures observed to calories, owing to the specific heats used, since the same solution and apparatus were used throughout the work, the results were strictly comparable one with another, and the

absolute values are probably not more than one or two per cent. above or below those recorded.

The method of making the determinations was to put in the weighed beaker a weighed amount, usually about 275 grams of potassium copper chloride. The beaker was then placed in the calorimeter, with the cover on, and allowed to come to constant temperature. Since the stock solution was always kept in the constant temperature room the beaker containing the solution did not have to stand in the calorimeter more than about half an hour before the sample of steel could be added.

The sample of iron or steel was prepared by filing, or pounding the metal when too hard to file, but in all cases was reduced to a powder, fine enough to pass through a sieve with seventy meshes to the inch. This fine subdivision was necessary in order to insure rapid solution. When the temperature of the calorimeter had become constant two grams of the finely divided iron or steel were introduced into the beaker, the cover being temporarily raised for this purpose, and the stirrer was started. Solution was rapid, the maximum temperature in almost all cases being attained within fifteen to twenty minutes. The usual rise was from  $5^{\circ}$  to  $7^{\circ}$ . In one case, when the time of solution was unusually prolonged, about forty minutes being required, an allowance was made for loss by radiation. With temperature of the beaker  $6^{\circ}$  above that of the initial temperature, this loss was found to be  $0.24^{\circ}$  per hour. This correction had to be made only in one case.

The method of subjecting the different steels to heat treatment was as follows: Steel to be annealed was placed as far as possible out of access of air and heated to a temperature of between  $900^{\circ}$  and  $1,000^{\circ}$  and cooled very slowly. Quenched or hardened specimens were prepared from pieces of the annealed metal. Pieces of the steel usually weighing from 50 to 100 grams were placed in a porcelain tube having an internal diameter of about twenty mm. This tube was wrapped with two layers of asbestos paper and slipped inside an iron tube which extended about thirty cm. beyond the end of the porcelain tube.

The center of the iron tube, the portion containing the specimen to be heated, passed through a Hoskins gasoline furnace in such a way that the tube for a distance of from fifteen to eighteen

cm. could be easily raised to any desired temperature up to  $1,200^{\circ}$  C. Through the porcelain tube was introduced the thermal couple of a Le Chatelier pyrometer, the thermal junction being in direct contact with the piece of steel under treatment. The pyrometer had been carefully graduated and we think the temperatures given are accurate within probably  $5^{\circ}$  or less. The other end of the iron tube was kept closed during the heating by a cork in order to avoid oxidation. When everything was ready the temperature of the tube was slowly raised, the time usually being from twenty to forty minutes until the pyrometer indicated that the bar was at the desired temperature. When this was attained the cork was removed from the end of the tube and by quickly tilting the latter the piece of steel was dropped into ice-water at a temperature of from  $4^{\circ}$  to  $5^{\circ}$ . After the operation corrections for the temperature of the galvanometer, etc., was made, and the actual temperature at the moment of tilting the tube was calculated.

The heat of solution of the various samples of steel is shown in the following tables, Table I showing the influence of composition and varying heat treatment on the heat of solution, Table II showing heat of solution of other samples. The numbers given in the tables are the averages of at least two duplicates; the difference between two determinations on the same sample seldom exceeded four calories and only in one case was it six :

TABLE I.

SHOWING INFLUENCE OF CHEMICAL COMPOSITION AND HEAT TREATMENT ON THE HEAT OF SOLUTION.

Experi- ment No.	Name of metal.	Chemical composition.					Heat treatment.	Calories evolved per gram of Fe + Mn.	
		C.	Mn.	P.	S.	Si.		Heat treatment.	Calories evolved per gram of Fe + Mn.
1	Pure iron wire	0.018	none	0.050	0.013	0.023	annealed	....	659.6
2	Car. H	0.09	0.22	0.016	0.023	....	"	....	629.1
3	" "	0.09	0.22	0.016	0.023	....	"	714 <sup>o</sup>	637.0
4	" "	0.09	0.22	0.016	0.023	....	"	825 <sup>o</sup>	650.9
5	" "	0.09	0.22	0.016	0.023	....	"	925 <sup>o</sup>	684.7
6	" "	0.09	0.22	0.016	0.023	....	"	1025 <sup>o</sup>	712.3
7	" "	0.09	0.22	0.016	0.023	....	"	1025 <sup>o</sup>	705.9
8	Cl. 5	0.10	0.484	0.119	....	....	annealed	....	632.9
9	" 5	0.10	0.484	0.119	....	....	"	719 <sup>o</sup>	651.2
10	" 5	0.10	0.484	0.119	....	....	"	825 <sup>o</sup>	676.0
11	" 5	0.10	0.484	0.119	....	....	"	928 <sup>o</sup>	707.6
12	" 5	0.10	0.484	0.119	....	....	"	1028 <sup>o</sup>	741.1
13	N. S. 5	0.37	0.820	0.160	....	....	annealed	....	587.3
14	" 5	0.37	0.820	0.160	....	....	"	728 <sup>o</sup>	626.3
15	" 5	0.37	0.820	0.160	....	....	"	827 <sup>o</sup>	652.2
16	" 5	0.37	0.820	0.160	....	....	"	923 <sup>o</sup>	675.1
17	" 5	0.37	0.820	0.160	....	....	"	1027 <sup>o</sup>	760.6
18	Car. I	1.22	0.780	0.098	0.068	0.058	annealed	....	635.1
19	" "	1.22	0.780	0.098	0.068	0.058	"	719 <sup>o</sup>	641.9
20	" "	1.22	0.780	0.098	0.068	0.058	"	750 <sup>o</sup>	686.6
21	" "	1.22	0.780	0.098	0.068	0.058	"	825 <sup>o</sup>	696.7
22	" "	1.22	0.780	0.098	0.068	0.058	"	923 <sup>o</sup>	717.3
23	" "	1.22	0.780	0.098	0.068	0.058	"	1023 <sup>o</sup>	755.6
24	T. S. D.	1.28	0.330	0.018	0.006	....	annealed	....	628.9
25	" " "	1.28	0.330	0.018	0.006	....	"	1025 <sup>o</sup>	693.0

TABLE II.  
HEATS OF SOLUTION OF OTHER SAMPLES.

Experi- ment No.	Name of metal.	Chemical composition.					Heat treatment.	Calories evolved per gram of Fe + Mn.
		C.	Mn.	P.	S.	Si.		
27	C. R. M. Co. 5	0.36	1.25	0.122	0.128	0.046	Normal.	560.7
28	Car. F.	0.55	0.70	0.027	0.026	....	Annealed.	562.0
29	" "	0.55	0.70	0.027	0.026	....	Hardened and reheated to 275 <sup>o</sup> .	639.4
30	Cast steel	0.76	0.27	0.017	trace	0.234		Annealed.
31	No. 5. Char. pig iron	c 1.70 g 1.95	trace	0.260	....	0.262	Normal.	620.0
32	Pure carbide of iron	6.64	none	0.026	....	....	Annealed.	647.3
33	Swed. bar iron	....	....	....	....	....	Normal.	670.0
34	Special iron	3.22	0.33	0.018	0.006	....	Poured while molten into cold water.	756.0
35	" "	3.±	0.33	0.944	0.006	....	Poured while molten into cold water.	798.0
36	Pure Cu. wire	...	....	....	....	....	Normal.	60.2
37	" " "	...	....	....	....	....	Cooled slowly from 1,000 <sup>o</sup> .	66.3
38	" " "	...	....	....	....	....	Quenched from 940 <sup>o</sup> .	58.2



The following points seem to be indicated by the results in Tables I and II.

*First.* In annealed metal, owing to the heat of formation of compounds of iron with carbon, the heat of solution diminishes as the per cent. of carbon increases, until after the saturation point (eight-tenths to nine-tenths per cent.) is passed, when, owing probably to the endothermic formation of non-crystalline cementite, the heat of solution increases again, but never reaches that of pure iron. This is shown in experiments 1, 2, 30, 24, 31.

The heat of solution of the last mentioned may be somewhat lowered by the presence of phosphorus and silicon, the decomposition of whose compounds would almost certainly absorb some heat.

*Second.* The presence of manganese, when combined with carbon in annealed metal, diminishes very markedly the heat of solution, owing to the greater stability of the compounds of manganese and carbon, compared with that of the corresponding compounds of iron. If there is not sufficient carbon to combine with the manganese, or if the carbon is above the saturation point, the substitution of manganese for iron seems to increase the heat of solution slightly, owing to the higher heat of formation of manganous chloride compared with that of ferrous chloride. This influence of manganese on heat of solution of annealed metal is clearly shown in experiments Nos. 2 and 8, 13 and 27; 28, 24, and 18.

*Third.* In the quenched metal, manganese seems to behave exactly the reverse from that in the annealed steel, the effect being to very notably increase the heat of solution, the increase being more marked the higher the temperature from which the steel is quenched. This is shown on comparing the heats of solutions of experiments Nos. 7 and 12, 17, 23 and 25.

*Fourth.* That phosphorus plays a considerable part in determining the heat of solution is shown by experiments 34 and 35, although these cannot be easily compared with the above, since the temperature from which the metal was quenched is not known, but must have been not far from  $1,100^{\circ}$  or  $1,200^{\circ}$ , as the metal was perfectly fluid when poured into cold water.

*Fifth.* The results obtained on copper (experiments 36, 37,

and 38) confirm those of Osmond, that is, that heat treatment has but slight influence on the heat of solution.

The next series of experiments undertaken was to determine the influence of reheating or "tempering" hardened steel upon its heat of solution. The steel selected for this purpose was the steel marked T. S. D. (see experiment 24, Table I). The steel had been hardened by heating to between  $900^{\circ}$  and  $1,000^{\circ}$  and quenching in ice-water. On account of the low phosphorus present in the metal we knew that it would be useless to attempt to get such steel as this in a sufficiently fine state of division for the work, if the metal was tempered before subdividing. High-grade tool steel of this class, if hardened and tempered, would be too hard to file and too tough to pulverize in a steel mortar, so that we resorted to the plan of pulverizing a considerable amount of the hardened metal and reheated the powdered steel in a stream of hydrogen or of nitrogen in order to avoid oxidation. For reheating to temperatures up to and including  $400^{\circ}$  from five to six grams of the bright powdered steel was placed in a large test-tube provided with a three-hole stopper; through one hole there was a tube for the purpose of conducting pure dry hydrogen nearly to the bottom of the test-tube; through the second hole a nitrogen filled thermometer was introduced, the bulb of the thermometer reaching to the bottom of the test-tube and being surrounded by the steel; the third hole was provided with a piece of tubing drawn down to a fine point, serving as an escape for the hydrogen.

For heating to  $100^{\circ}$  C. the test-tube so arranged was kept in a water-bath for twenty-four hours, the air in the test-tube having been displaced by pure dry hydrogen. For raising the temperature to from  $200^{\circ}$  to  $400^{\circ}$ , inclusive, the following device was employed: A piece of pig iron weighing about five kilos was drilled nearly through, the hole being somewhat larger than the diameter of the test-tube used. A little sand was placed in the hole, then the test-tube inserted deep enough so that the steel was a little below the center of the bar; the space around the test-tube was then filled with sand. This arrangement secured the slow, even heating of the sample. When the air in the test-tube had been completely displaced by dry hydrogen, the bar was slowly heated until the thermometer indicated the desired

temperature. The light was then turned out and the tube allowed to cool in hydrogen. For temperatures higher than 400° the powdered steel was placed in a porcelain combustion boat contained in a porcelain combustion tube. One end of this latter was closed by a one-hole stopper through which the dry hydrogen or nitrogen employed was conducted. In the other end of the combustion tube the thermal couple of the pyrometer was introduced in such a way that the thermal junction rested on the boat containing the steel. The portion of the tube containing the boat was then slowly heated in an ordinary combustion furnace, or for higher temperatures in a gasoline furnace, until the desired temperature was attained, then allowed to cool, the current of hydrogen or nitrogen being kept up during the cooling. Bright powdered steel underwent no apparent change in color, only when heated to 1,024° the mass showed a slight tendency to stick together.

In addition to determining the heat of solution of these reheated samples, we made colorimetric carbon determinations, using the annealed steel carbon, 1.28 per cent., as a standard.

The results of the reheating on the heat of solution and the color carbon determinations are embodied in Table III.

TABLE III.

SHOWING INFLUENCE OF TEMPERING ON HEAT OF SOLUTION AND COLOR CARBON TEST.

Experiment No.	Temperature to which metal was raised.	Gas used.	Calories evolved per gram Fe + Mn.	Carbon indicated by color.
39	0		688.0	1.14
40	100°	Hydrogen	685.8	1.14
41	200°	"	685.8	1.14
42	250°	"	673.9	1.14
43	300°	"	666.0	1.18
44	400°	"	662.5	1.20
45	500°	"	657.6	1.27
46	609°	"	634.7	1.27
47	715°	"	631.8	1.16
48	739°	"	687.4	1.03
49	1024°	"	705.6	0.29
50	1024°	Nitrogen	583.3	0.57
51	1024°	"	560.6	0.73

It will be noticed in this table that the heat of solution decreases and the apparent per cent. of carbon increases with

the temperature to which the metal is reheated until the critical point  $A_c$  is passed. When the critical point  $A_c$  is passed the hydrogen seems to combine with the carbon and the heat of solution rises very markedly. When the gas used was nitrogen, the temperature being over  $1,000^\circ$ , the nitrogen removes the carbon, part at least forming cyanogen, as was shown by passing the nitrogen through potassium hydroxide and precipitating silver cyanide with silver nitrate, after acidification with nitric acid. The heat of solution of the metal heated and cooled in nitrogen is very much lowered, being in fact what we might expect of ordinary annealed metal of the indicated per cent. of carbon, as brought out in Table I.

Why iron heated to high heats in hydrogen and cooled in this gas should increase the heat of solution, we are not at present prepared to state, but we hope to investigate this point in the near future.

The last set of experiments was made to show the influence of cold working upon the heat of solution and tensile strength of pure iron. The sample used was one of very fine No. 36 pure, bright iron wire twenty-two hundredths mm. in diameter and of the composition shown in experiment No. 1. In subjecting this to heat treatment small coils of the wire were placed in a porcelain combustion tube and slowly raised to the temperature indicated, as shown by the Le Chatelier pyrometer, a current of dry hydrogen being kept up during the operation.

As in the work on reheating powdered steel the metal was cooled in a current of hydrogen, after being heated to the desired temperature. After the heat treatment a portion of the metal was used for making tensile strength determinations and part was dissolved for determining the heat of solution. The results of this work are given in Table IV.

TABLE IV.  
SHOWING EFFECT OF REHEATING ON HEAT OF SOLUTION AND TENSILE STRENGTH OF COLD DRAWN IRON WIRE.

Experi- ment. No.	Temperature to which wire was raised.	Calories evolved per gram of Fe + Mn.	Tensile strength.	
			Kilos per square mm.	Pounds per square inch.
52	0	802.1	96.8	135,520
53	$400^\circ$	750.6	74.2	103,880
54	$609^\circ$	663.9	42.1	58,940
55	$765^\circ$	659.6	....	....

The following interesting relation is brought out in the above table. The diminution in tensile strength is almost exactly proportional to the diminution in the heat of solution. Thus, in reheating to 600° the heat of solution has fallen from 802.1 to 663.9, or 138.2 calories, while the tensile strength has fallen from 96.8 to 42.1, or 54.7 kilos per square mm., or the tensile strength has been reduced at the rate of 0.395 kilos per square mm. for each calorie diminution in the heat of solution. That this holds very nearly, is shown by the results obtained by reheating to 400°. The heat of solution has diminished 51.5 calories, which, if the tensile strength diminishes proportional to the falling off in the heat of solution, would indicate a tensile strength of 76.46 kilos, whereas the actual results gave 74.2 kilos.

If the increase in tensile strength accompanied by increase in heat of solution of this wire is due to allotropy in the iron induced by cold working, then the hardening of steel cannot easily be attributed to the same allotropic change, since the drawn iron wire has a higher heat of solution and hence presumably a higher proportion of non- $\alpha$ -iron than any of the hardened steels, and yet the wire is comparatively very soft, while many of the steels are hard enough to scratch glass easily.

Although a number of interesting facts have been brought out in the above work, the data obtained are yet too few to enable reliable conclusions to be drawn in regard to phenomena complicated by so many factors as are present in the work under examination.

We hope to continue the work along the lines indicated in the present paper and to obtain results more satisfactory than those herein described.

ANN ARBOR, MICH., June 24, 1897.

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#### NOTE.

The Fifteenth Annual Report of the Committee on Indexing Chemical Literature, just received from the chairman, Dr. Bolton, shows very great progress. Dr. Bolton's pioneer work has borne good fruit. Most books on chemistry now issued make some attempt at a bibliographic account of the subject-matter greatly to the benefit and convenience of the reader. Copies of the report may be obtained of the chairman, Dr. H. Carrington Bolton, Cosmos Club, Washington, D. C.