

ON THE CARBURISATION OF IRON.

II.

IN a previous communication (NATURE, vol. xlv. p. 283) the problem of the distribution and absorption of carbon by iron has been discussed, and it has been shown that the process is akin to that of the solution of a salt soluble in water or an acid liquid, that at low temperature solution proceeds slowly, the solubility increasing with the temperature, until at the final high heat of Bessemer blown metal, or fluid nearly pure iron, the reaction is almost instantaneous; the carbon, and also manganese, contained in the spiegel-eisen used for this purpose diffusing throughout the fluid metal in a very short space of time. The same occurs when carbon only, in the form of charcoal or coke, is added in lieu of spiegel, as in the Darby process of carburising. By this latter process, however, about 30 per cent. excess of carbon must be added over and above the theoretical quantity required to insure a given percentage of carbon, for instance, $\frac{1}{2}$ per cent. For lower percentages the excess must still be maintained, but with a corresponding diminution of the total weight of carbon used. In some instances more than 30 per cent. is used, according to the methods of procedure. In practice this holds good and the quantity of carbon required can thus be regulated.

A priori this would seem impossible. An excess 30 per cent. above the quantity necessary being used, it seems strange that, at the high temperature in the presence of a considerable excess of fluid metal, that nearly the whole of the carbon is not taken up, more especially when iron, as is well known, may absorb as much as 5 per cent. of carbon in the blast furnace; usually, however, cast iron contains not more than 4 and spiegel eisen 5 per cent. carbon, the latter alloy of manganese and iron apparently conferring greater solubility. It even suffices to pour the fluid metal on the pulverised carbon previously placed in the ladle, and a very even product is thus obtained, sufficing for all practical purposes, the variation in the percentage of carbon absorbed or dissolved falling within the limits of experimental error. It is possible that after absorption of carbon equalling say $\frac{1}{2}$ per cent., if the iron were left in contact with carbon for a longer period, more might be taken up; and that with iron already charged with carbon, solution may be retarded; the rate at which the latter is taken up probably bearing a certain ratio to the amount previously absorbed. If carbon simply exists in solution this is very probable, and yet the theory would hardly afford at first sight a feasible explanation of the even absorption of carbon which thus takes place, were it not well known that most chemical reactions, so to speak, fall into the same category.

Chemical affinities are not entirely governed by actual values; or the affinity of one element for another; the mass or relative weight of the bodies present influences the final result; and it is conceivable that, assuming we have two bodies in solution, the addition of a reagent having a greater affinity for one of these may not, in the presence of an excess of the other, exert its full power, the greater mass or weight of the latter apparently weakening, or rather partly neutralising, the chemical force of the reagent added.

Further cases can be quoted where relative masses in solution are so evenly balanced that a slight excess of the reagent added determines the precipitation of one or the other at the will of the operator.

Barium sulphate is somewhat soluble in acids, and by prolonged digestion a portion is dissolved. Either barium or sulphuric acid may be precipitated by merely, as regards barium, adding a slight excess of sulphuric acid. On the contrary the addition of a little barium chloride determines the precipitation of sulphuric acid. Apparently,

then, excess or mass of one element overcomes the greater affinity of the other for the reagent added, or, as often happens, a portion is left uncombined and in solution, requiring an excess of the reagent for the complete precipitation or combination.

Such cases as those above quoted are not uncommon in metallurgical processes conducted at high temperatures. Thus in the case of the manufacture of Bessemer steel, analysis indicates the presence of diverse elements existing together.

One has—silicon, carbon, hydrogen, oxygen, manganese—also sulphur and phosphorus together with, it is said, carbon monoxide in solution—also probably dissolved oxygen in addition to iron oxide. Further, steel with more than $\frac{1}{2}$ per cent. of carbon, and also silicon and manganese in sensible quantities, always contains O and H; and thus we have the elements of water side by side in the presence of a tolerable excess of no less than three bodies, Si, C, and Mn, having affinities for oxygen.

It is quite true that the abnormally high temperature of the process may weaken ordinary chemical reactions by a species of dissociation; this has been acknowledged. Yet mass or relative proportions of the elements present must, one would think, influence final results, and thus prevent the complete elimination of the elements named for the reasons already stated.

The treatment of fluid iron with reagents such as C, Si, Mn, or alkalis, as now practised, is as strictly a chemical process as that pursued by the chemist in his laboratory. In both, reagents are employed which are known to be suitable for the elimination or precipitation of substances known to be present; and, so far as can be ascertained from actual practice, the steel-caster deals with molten metal containing certain elements in solution, and endeavours to get rid of some of these, or adds others assumed to be beneficial, just as the chemist works with solutions known to contain bodies possibly existing or combined with the fluid solvent in much the same manner as the worker with fluid iron. There seems but little difference, take it as one may; the same laws of combination, solution, &c., seem equally applicable; and differences of opinion as to what is really meant by the terms solution, chemical combination, or simply mixtures, are common to both. Further, it must not be forgotten that pure fluid iron, although exerting a direct solvent action on certain bodies, may take up or dissolve a chemical combination or double salt, just as pure water does. This, however, remains an open question, but it would be interesting to know if certain combinations of iron with other elements are thus held in solution.

As regards carbon there can be little doubt of the existence of definite carbides of iron; and it may be that combinations of iron with bodies other than carbon may play a part. Some recent work on certain alloys of iron points to the probability of the formation of these. Assuming the presence of a definite carbide of iron which may not be in solution, but diffused evenly throughout the fluid iron, although we cannot be absolutely sure of this, the behaviour of steel under certain conditions of heating and manipulation may be explained on the assumption that iron carbide, being certainly more fusible than pure iron, must become soft and plastic at a temperature at which the mass of pure metal is scarcely at all affected. This plastic compound would bind the non-coherent particles of the greater mass of iron together, and this mixed or heterogeneous body could be welded or beaten out under the hammer. It is the general opinion that the weldable metals are mixed bodies, are not homogeneous, inasmuch as bodies purely homogeneous cannot as a rule be welded together.

Wrought iron welds easily, far more easily than steel, and it is certain that the former is not homogeneous, whatever may be said of the latter. Wrought or puddled iron is well known as an irregular mixture, composed of grains

of pure metal intermixed with carburised metal, and also slag. The latter is said to play its part in rendering the total mass more coherent when heated and worked. This latter material when fused and cast into ingots is a totally different material, and behaves somewhat like steel. If this now comparatively homogeneous substance contain enough carbon (which sometimes is not the case; in the latter instance it is brittle and redshort, behaving somewhat like Bessemer blown metal) it works like a soft steel.

It follows, therefore, that if fusible compounds are present, and evenly diffused throughout the pure metal, their effect on steel is purely physical, and a heterogeneous metal like steel may be compared with rocks, which are known to be composed of siliceous particles, cemented or bound together by other compound bodies. Dr. Sorby long ago noted this, and drew attention to the comparative uselessness of ordinary chemical elementary analysis, simply stating the percentage of elements present, and suggested that proximate analyses were equally required. The writer is fain to agree with him, his own experience of the comparative failure of ordinary analysis as a trustworthy guide in the manufacture having been somewhat extensive. The purest form of iron known to the writer is the Bessemer blown metal, beyond traces of carbon, with less than $\frac{1}{10}$ th per cent. of sulphur and phosphorus. It is pure iron (with some kinds of iron only traces of these latter can be detected). This metal is worthless for commercial purposes, and this is said to be due to the presence of oxide of iron or possibly dissolved oxygen absorbed during the blow; to a certain extent this has been proved to be true. But the writer thinks that on the whole the pure material, even when freed from oxygen, would be commercially valueless, and if, shortly speaking, the cement theory or mixture of bodies (the one more fusible than the other), be true, pure iron is unworkable.

The opinions quoted are apparently not in accord with the theory of solution previously summarised, and leave unexplained the undoubted fact of the diffusion or solution of carbon in iron at low temperatures, tending, of course, if time be allowed, to the formation of a homogeneous material. Yet a carbide of iron is known, " Fe_3C ," and has been isolated. It appears to the author that one somewhat reasonable explanation of this anomaly has been afforded by W. Mattieu Williams. He compares the union of carbon and iron to the processes of tinning or galvanising. If a plate of copper is immersed in melted tin a film of tin adheres to its surface, and if continued the tin will gradually soak into the copper, and in time will go through. Tin or zinc penetrates iron in the same way; mercury also amalgamates with copper; therefore carbon (Fe_3C) may be similarly distributed in iron.

This may or may not be the case, but in the author's opinion it does not meet all the difficulties, or afford a complete explanation of the phenomena taking place when iron is heated and worked in contact with carbon. Neither does the alternative theory of solution, either in the ordinary sense of the word or, better, as defined by modern physicists, afford a complete explanation. Yet on the whole the latter seems to afford a better and more complete all-round explanation of some curious changes observable when steel is heated up to certain varying temperatures, the results of which are now familiar to us.

Referring once again to the curious fact of the even distribution of carbon throughout iron, when plates of uneven composition as regards the percentage of carbon are heated together, it appears as the outcome of recent research¹ that chemical action, "or something closely approximating to it," takes place between solids, and even at low temperatures. Many experiments are given—thus

dry ice and rock salt unite when placed in contact at a temperature decidedly below zero.

This is a very old experiment, but it is interesting as an example of the union of two solids below the fusing point of either, but above that of the product. He obtained similar results in other cases with sodium, potassium, calcium, and ammonium chloride, &c. This suggests the question, Are the metals combining to form an alloy "in the new way," *i.e.* in the form of solids, a freezing mixture?

Space does not admit of further quotation; the fact remains that solids combine with solids to form an alloy, or possibly what is termed a chemical combination.

At first sight this seems inconceivable and irrational. Many alternative theories and explanations of these curious phenomena are at our disposal. Yet there remains one simple way of accounting, at least in some degree, for this alloyage—or one ought perhaps to say the interpenetration of one element into another, as with carbon and iron. It is now, we think, generally admitted, in the light of recent researches on the vaporisation of the elements, "both in vacuo and at ordinary pressures," that no known element, however infusible, can be said to be perfectly stable at any temperature when freely exposed in space; and it is extremely probable that even such substances as iron and carbon are slowly dissociating at ordinary temperatures very much as water evaporates, and it follows that these are always enveloped in a thin atmosphere of their own vapour. The quantity of matter present in this form may never be recognisable; it may indeed be beyond the limit of our senses. Yet if such a process takes place, it affords a probable explanation of the diffusion of solids into each other. For admitting this it is evident that any mass or mixed masses of matter exist in an atmosphere formed by themselves. Such masses of matter cannot be discontinuous, strictly speaking, the sensible particles of which they are composed are not completely isolated from each other, and from this point of view the conception of the interpenetration of iron by carbon, or indeed other bodies, is, one thinks, rendered more easy.

JOHN PARRY.

NOTES.

BOTANISTS all over the world will be sorry to hear of the death of the famous Swiss botanist, Alphonse de Candolle. He was in his eighty-seventh year. We hope to give on a future occasion some account of his services to science.

WE regret to hear, through the *Botanical Gazette*, of the death of the Rev. T. Wolle, pastor of the Moravian Church, Bethlehem, Pennsylvania, an ardent student of freshwater algæ. Of his three most important publications, "Freshwater Algæ of the United States," "Desmids of the United States," and "Diatoms of the United States," at least the first two will always be standard works in the subject of which they treat.

THE ordinary general meeting of the Institution of Mechanical Engineers will be held on Thursday evening and Friday evening, April 21 and 22, at 25, Great George Street, Westminster. The chair will be taken at half past seven p.m. on each evening by the president, Dr. William Anderson, F.R.S. The following papers will be read and discussed, as far as time permits:—Second report to the Alloys Research Committee, by Prof. W. C. Roberts-Austen, F.R.S. (Thursday, and discussion possibly continued on Friday); tensile tests and chemical analyses of copper plates from fire-boxes of locomotives on the Great Western Railway, by Mr. William Dean (in connection with the above report); Research Committee on marine-engine trials: abstracts of results of experiments on six steamers, and conclusions drawn therefrom in regard to the efficiency of marine boilers and engines, by Prof. T. Hudson Beare. The anniversary dinner will take place on Wednesday evening, April 19.

¹ William Hollock, *American Journal of Science*, vol. xxxvii. 1889.