

CHAPTER V.

THE CHEMISTRY OF THE BASIC BESSEMER PROCESS.

Acid and Basic Process Contrasted.—The removal of the Carbon, Silicon, and Manganese in the basic Bessemer process, is exactly the same as in the acid Bessemer, except that the removal of the Silicon is more complete. The real difference between the processes commences after the removal of the Carbon, at the drop of the flame, as, on continuing the blowing, the Phosphorus is attacked, and combines with the lime in the slag to form a stable Phosphate of Lime. This continuation of the blow after the removal of the Carbon is known as the "after blow," and before this stage is reached the Phosphorus is removed to a very slight extent only. The elimination of Phosphorus depends upon the fact that, at the temperature of the converter, Phosphate of Lime is not decomposed by metallic iron.

In the acid process the removal of Phosphorus is impossible, because Phosphate of Iron, assuming it to be formed in the presence of a silicious slag and molten iron, is immediately decomposed, and the Phosphorus passes back into the metal. The basic lining theoretically takes no part in this reaction, except in so far as it provides a non-silicious lining, and enables a very basic slag to be formed by additions of lime; but a neutral lining of Chrome iron ore, or similar material, would—provided it could resist the high temperature and mechanical abrasion of the metal, and if lime were added, in sufficient excess to combine with the Phosphorus, Silica, &c.—answer the same purpose. Part of the lining is always fluxed and part is abraded, thus assisting to form the slag, but this is accidental; and the object of making lime additions is to form a basic slag as early in the blow as possible, and so protect the linings of the vessels from this action.

The amount of lime that is added must vary with the composition of the metal; the more silicious and Phosphoric the pig-iron, the larger the quantity of lime required.

Pig-Iron Requirements for Basic Practice.—A good basic pig for Bessemer work should contain about 0.50 per cent. of Silicon, and never more than 1.00 per cent. As sulphur is removed only to a limited extent during the basic blow, and as its removal is somewhat erratic, it is necessary, in making basic pig, either to smelt Manganiferous iron ore, or to mix some Manganese ore with the blast furnace burden, to insure obtaining a pig iron low in sulphur; with the result that the best pig-iron of this class usually contains about 2 per cent. of Manganese. The percentage of Phosphorus is important, as in working with a low Silicon pig-iron, Phosphorus, Manganese, and Carbon are the only elements relied upon as fuel for raising the bath of metal to the required temperature for teeming. In other words, a certain percentage of Phosphorus is as essential to the basic Bessemer as a certain percentage of Silicon is to the acid Bessemer. In actual practice, about 2.5 to 3.00 per cent. of Phosphorus in the pig-iron is found to give the best results, as with a lower percentage than this, unless the Silicon is high, there is considerable danger of getting "cold heats." Pig-iron containing

much less Phosphorus than this has been frequently employed, but it does not give satisfactory results. Another important point with reference to Phosphorus is the question of the percentage of Phosphoric Acid in the slag, for, apart from any metallurgical considerations, it is of vital importance, from a commercial point of view, to obtain a slag rich in Phosphoric Acid, as otherwise its value for agricultural purposes is greatly reduced.

Purity of the Lime.—It is very important that the lime employed should be as free as possible from Silica, as every pound of Silica may be said in general terms to require 4 lbs. of lime to flux it, so that each per cent. of Silica in the lime entails a loss of 5 per cent. on the weight of lime added, and it also appears to retard the removal of sulphur. In many works lime, with Silica not exceeding 1 to 1.5 per cent., is used, although generally it amounts to 2 per cent., and sometimes considerably more.

Oxidation of Impurities.—The following series of analyses by Stead (Table xv.) of metals and slags taken during a low Phosphoric basic Bessemer blow, show the general changes taking place, and the curve, in fig. 86, which has been deduced from a number of published and private analyses, shows graphically the gradual oxidation of the impurities with more Phosphoric iron:—

TABLE XV—ANALYSES OF METAL TAKEN AT DIFFERENT PERIODS OF THE BASIC BESSEMER PROCESS.

| Period from Commencement. | Carbon. | Manganese. | Silicon. | Sulphur. | Phosphorus. | Copper. |
|---------------------------|-----------|------------|-----------|-----------|-------------|-----------|
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Fluid Iron, - | 3.57 | 0.71 | 1.70 | 0.06 | 1.57 | Trace. |
| 3 mins., - | 3.68 | 0.62 | 0.81 | 0.06 | 1.60 | " |
| 6 " - | 3.40 | 0.56 | 0.28 | 0.06 | 1.63 | " |
| 9 " - | 2.35 | 0.38 | 0.05 | 0.05 | 1.43 | " |
| 12 " - | 0.88 | 0.27 | 0.01 | 0.05 | 1.42 | " |
| 14½ " - | 0.07 | 0.12 | Trace. | 0.05 | 1.22 | " |
| 16½ " - | Trace. | 0.10 | Nil. | 0.05 | 0.14 | " |
| 16 " 35 secs., | Trace. | Trace. | Nil. | 0.05 | 0.08 | " |

ANALYSES OF SLAG TAKEN AT DIFFERENT PERIODS OF THE BASIC BESSEMER PROCESS.

| | Silica. | Phosphoric Acid. | Metallic Iron. |
|------------------|-----------|------------------|----------------|
| | Per cent. | Per cent. | Per cent. |
| 3 minutes, - | 32.60 | 0.60 | 5.65 |
| 6 " - | 42.60 | 1.15 | 2.00 |
| 9 " - | 36.00 | 1.60 | 4.60 |
| 12 " - | 35.60 | 2.61 | 4.80 |
| 14 " 30 seconds, | 33.00 | 5.66 | 6.15 |
| 16 " 30 " - | 15.60 | 15.06 | 10.45 |
| 16 " 35 " - | 16.60 | 16.03 | 11.35 |

The analyses were made from fused slag, not from a mixture of lime and scoria.

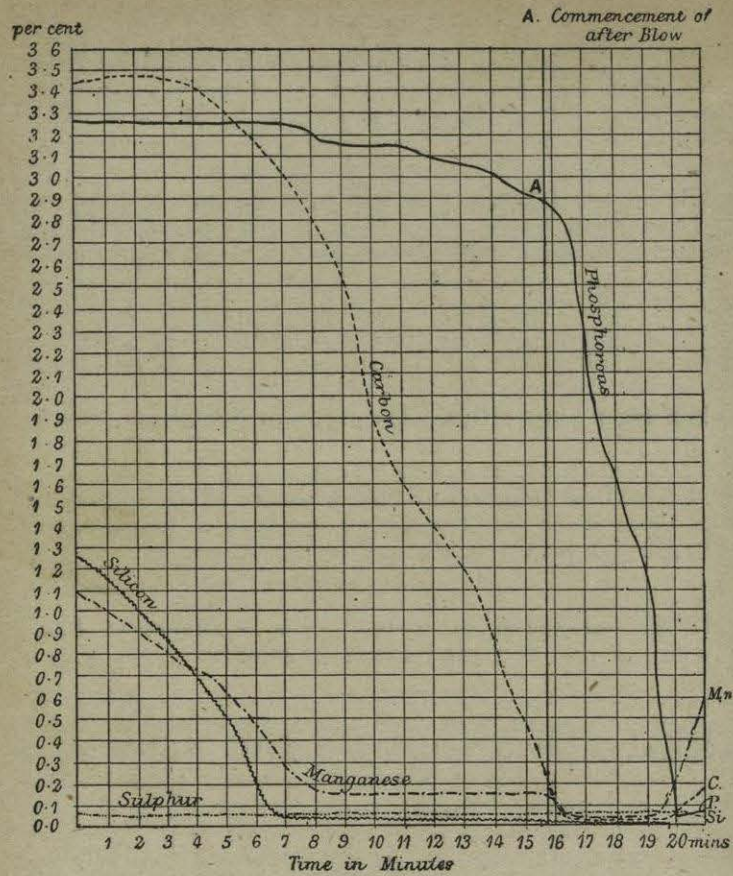


Fig. 86.

Silicon and Manganese.—The Silicon is the first of the constituents to be attacked during the blow, and is almost entirely oxidised during the first few minutes—i.e., before the Carbon begins to disappear rapidly. The Silicon is much more completely removed than in the acid process, probably in part owing to the lower temperature resulting from the addition of considerable quantities of lime, and also to its affinity for so strong a base as the latter. Manganese passes out rapidly from the commencement of the

| BLOW No. | DESCRIPTION. | IN METAL. | |
|----------|--|-----------|-------|
| | | Mn. | P. |
| 184 | Disappearance of spectrum line—i.e., commencement of after-blow, - - - - - | 0.19 | 2.070 |
| | Second lime addition, - - - - - | 0.62 | 0.463 |
| 185 | Disappearance of spectrum line, - - - - - | 0.24 | 2.180 |
| | Second lime addition, - - - - - | 0.81 | 0.718 |
| 186 | Disappearance of spectrum line, - - - - - | 0.24 | 2.390 |
| | Second lime addition, - - - - - | 0.79 | 0.483 |

blow, but is not so completely removed as in the acid process. Stead * has shown that Phosphide of Iron is capable of reducing Oxide of Manganese when the two are melted together in a basic-lined crucible, and the above results given by Wedding † show that Manganese is reduced from the slag, and passes back into the metal during the basic after-blow, although it is to a great extent re-oxidised before its termination (see table, p. 94).

It can hardly be assumed that, under the oxidising conditions existing during the after-blow, Oxide of Manganese is reduced, but on stopping the blast and adding lime it appears that either the Phosphide of Iron present, or the mass of iron at the high temperature has a greater affinity for Oxygen than the Manganese, and these are able to act as reducing agents. From Stead's experiment, quoted above, it seems probable that the Phosphide of Iron, in the presence of large excess of lime, acts as the reducing agent.

Although the author has never verified this passing back of Manganese in the basic converter, he has done so repeatedly in the basic Siemens process, and there is no doubt that, owing to the presence of a powerful base like lime, the Oxide of Manganese is much more readily reduced from the slag than it is from the silicious slag in the Bessemer acid process.

Sulphur and its Elimination.—The behaviour of Sulphur during the blow is somewhat erratic, in certain cases a considerable proportion being removed, while at other times the elimination is hardly perceptible. The percentage removed is much more marked in cases of charges high in Sulphur than in those low in Sulphur, but the conditions most favourable are somewhat difficult to determine, and the results obtained by numerous metallurgists vary greatly when working under apparently similar conditions.

C. H. Ridsdale, after a long experience at the North-Eastern Steel Coy.'s Works, states that with pig-iron containing 1½ per cent. of Manganese, 0.09 per cent. of Sulphur is reduced to 0.06 per cent., and this confirms the author's experience. Stead ‡ has summarised the results of various investigators, as to the removal of Sulphur in basic Bessemer from pig-iron containing different percentages as follows:—

| Sulphur in Pig. | Sulphur in Steel. | Percentage of Sulphur Removed. |
|-----------------|-------------------|--------------------------------|
| 0.420 per cent. | 0.150 per cent. | 64 per cent. |
| 0.307 " | 0.085 " | 73 " |
| 0.160 " | 0.100 " | 37 " |
| 0.090 " | 0.060 " | 33 " |
| 0.050 " | 0.050 " | Nil " |

Stead § found that fluid Oxides of Iron remove Sulphur from iron without the formation of Sulphur Dioxide, and he has also brought experimental evidence to show that the Sulphur in Sulphide of Iron is, in the presence of a fluid calcareous slag, converted into Calcium Sulphide. He contends that this is the reaction which takes place in the converter, the whole of the Sulphur being retained by the slag. Wedding|| on the

* *Iron and Steel Inst. Journ.*, 1893, vol. i., p. 66.

† *Ibid.*, 1890, vol. ii., p. 539.

‡ *Ibid.*, 1892, vol. ii., p. 283.

§ *Ibid.*, 1893, vol. i., p. 49.

|| *Ibid.*, 1890, vol. ii., p. 539.

other hand, distinctly states that a considerable amount of Sulphur is volatilised during the blow, and that the total percentage of Sulphur in the original charge of metal is not accounted for by the percentage of Sulphur found in the slag. This statement refers to high sulphur charges, and as no data are given it is impossible to say on what evidence it is based; but coming from so high an authority it must be assumed that it can be supported by experimental evidence. It is possible that both authorities are right and that whereas, under normal conditions of work, with a highly basic slag, and when dealing with metal containing Sulphur under 0.20 per cent., as in Stead's experiments, the whole of the Sulphur may be found in the slag; with a less basic slag and higher Sulphur contents in the bath of metal some of the Sulphur may escape.

Wedding's results confirm those of Stead as to the removal of Sulphur taking place almost entirely during the "after-blow," and he cites one instance where desulphurisation was greatly increased by prolonging the "after-blow" slightly after complete dephosphorisation, which supports the contention that the Oxide of Iron formed plays an important part in the elimination.

Hilgenstock * disputes the deductions drawn by Stead, and maintains that Sulphate of Lime is produced in the Bessemer converter, and that the irregular removal of Sulphur in the basic Bessemer is due to the decomposition of this Sulphate by the iron bath and its re-absorption by the molten metal. In the author's opinion Stead has proved his case, at all events so far as to show that the final result is that Sulphide of Calcium is produced in the basic converter, and Sulphur retained in the slag in that combination. In whatever form the Sulphur may be removed, it has been clearly shown by Messrs. Wedding, Stead, Ridsdale, and others that its removal takes place practically during the "after-blow;" this is just what might be expected, as then there is the production of Oxide of Iron in excess, a very high temperature in the bath, and at the same time a very fluid calcareous slag.

In the early stages of the blow the Oxides of Iron produced are rapidly reduced by the Carbon, Silicon, &c., and to a less extent by other constituents present, and the temperature of the converter is such that only a comparatively small part of the lime has as yet been dissolved in the slag, so that a fluid calcareous slag is not formed until the "after-blow." There is no doubt that the fluidity of the slag plays a most important part both in desulphurising and dephosphorising, and it is probably largely due to the fluidity that the presence of Calcium Chloride confers on the slags that the Saniter desulphurising process owes its success.

TABLE XVI.—ANALYSES OF METAL.

| Description. | Metal. | 1st Period. | 2nd Period. | 3rd Period. | 4th Period. |
|-----------------|-----------|----------------|---------------|-----------------|-------------|
| | | Desiliconised. | Decarburised. | Dephosphorised. | Steel. |
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Carbon, - - - | 2.32 | 2.180 | 0.07 | 0.02 | ... |
| Manganese, - - | 0.66 | 0.200 | 0.09 | 0.06 | ... |
| Silicon, - - - | 1.57 | 0.300 | 0.07 | Trace. | ... |
| Sulphur, - - - | 0.16 | 0.148 | 0.16 | 0.08 | 0.070 |
| Phosphorus, - - | 1.85 | 1.920 | 1.53 | 0.04 | ... |

* *Stahl und Eisen*, Jan. 15, 1893.

CORRESPONDING SLAGS.

| Description. | 1st Period. | 2nd Period. | 3rd Period. | 4th Period. |
|--|----------------|---------------|-----------------|-------------|
| | Desiliconised. | Decarburised. | Dephosphorised. | Steel. |
| | Per cent. | Per cent. | Per cent. | Per cent. |
| Lime, - - - - | 44.30 | 47.00 | 46.78 | ... |
| Magnesia, - - - | 0.72 | 0.86 | 1.80 | ... |
| Manganous Oxide, - - | 6.60 | 4.46 | 2.51 | 10.79 |
| Ferrous Oxide, - - - | 4.38 | 8.23 | 14.02 | 9.00 |
| Ferric Oxide, - - - | 1.29 | 1.00 | 4.29 | 2.14 |
| Alumina, - - - - | 0.35 | 0.26 | 0.30 | ... |
| Silica, - - - - | 39.20 | 29.80 | 14.90 | ... |
| Phosphoric Anhydride, - | 2.61 | 7.83 | 14.86 | ... |
| Sulphur, - - - - | 0.16 | 0.10 | 0.36 | 0.36 |
| Phosphorus, - - - | 1.14 | 3.41 | 6.49 | ... |
| Probable per cent. of liquid slag on 100 parts of metal, - - - - | 7 | 11 | 27.00 | ... |

Sulphur in lime used = 0.054 per cent.

The foregoing analyses by Stead (Table xvi.) from samples supplied by J. P. Walton show the removal of impurities during the basic blow with special reference to that of Sulphur. They also show that the entire amount of Sulphur present in the metal can be accounted for in the slag.

Assuming that the weight of slag per cent. of metal used was as given, we have the following sulphur account up to the end of the after-blow:—

| SULPHUR IN SLAG. | Sulphur. Per cent. |
|---|-----------------------|
| 27 per cent. of slag, at 0.36 per cent. Sulphur, | 0.097 |
| Less Sulphur added in the lime, 15.2 per cent., at 0.054 per cent. Sulphur, | 0.008 |
| Total received from metal, | 0.089 |
| | |
| SULPHUR REMOVED FROM METAL. | Sulphur. Per cent. |
| 100 parts of raw iron contained, | 0.160 |
| Less 85 parts of blown metal, at 0.080 per cent. Sulphur, | 0.068 |
| Total removed, | 0.092 |

The Sulphur removed during the fore-blow, calculated from the analyses of the slags, is as follows:—

| AFTER FIRST PERIOD. | |
|--|------------------------|
| The Sulphur in 7 per cent. slag, at 0.16 per cent. Sulphur, less 0.025 carried in by the lime, is equal to, | 0.009 on 100 of metal. |
| | |
| AFTER SECOND PERIOD. | |
| The Sulphur in 11 per cent. slag, at 0.10 per cent. Sulphur, less 0.026 carried in by the lime, is equal to, | 0.008 on 100 of metal. |

The following results, obtained by C. H. Ridsdale, of the North Eastern Steel Works, have confirmed the above:—

| Description. | Sulphur in Metal. | Sulphur in Slag. |
|---|-------------------|------------------|
| | Per cent. | Per cent. |
| 1. Metal poured into vessel, - - - - | 0·100 | ... |
| 2. After blowing five minutes, - - - - | 0·118 | ... |
| 3. At the drop of flame, - - - - | 0·118 | ... |
| 4. At first sampling, - - - - | 0·074 | 0·377 |
| 5. At finish of blow before adding Ferro-Manganese, - - - - | 0·071 | 0·391 |
| 6. Steel taken fifteen minutes after No. 5, - - - - | 0·057 | 0·480 |

It has been experimentally shown by Finkiner,* and confirmed by Hilgenstock and Stead, that Sulphate of Lime is decomposed by iron at high temperature, and indirectly this has an important bearing on the elimination of Sulphur in basic Bessemer practice, as when impure lime containing appreciable quantities of Sulphate of Lime is used for making additions, not only is no Sulphur removed from the metal, but some Sulphur actually passes from the slag into the metal. The importance of using a pure lime in this connection was pointed out by Mr. J. P. Walton,† who considers that the removal of Sulphur in the Bessemer converter largely resolves itself into a question of the purity of the lime employed. He found that with a non-silicious lime low in Sulphur, Sulphur was removed from the metal, while with a silicious lime high in Sulphur, the latter element passed from the slag into the metal. With lime containing from 2·5 to 3·5 per cent. of Silica, and 0·27 to 0·35 per cent. of Sulphur, he found, as the result of three experiments, that there was practically no elimination of Sulphur from the bath; but with an exceptionally pure lime, containing 0·4 per cent. of Silica and only traces of Sulphur, the Sulphur was reduced from 0·064 to 0·02, and 0·03 per cent. in the finished steel. On the other hand, he found that when compelled to use a lime containing 5 to 6 per cent. of Silica and 0·7 to 1·00 per cent. of Sulphur, the Sulphur increased from 0·06 per cent. in the cupola metal to 0·13, and even 0·20 per cent. in finished steel. The author's experience at the Staffordshire Steel and Ingot Iron Co.'s Works completely confirmed Mr. Walton's results, as under ordinary conditions a very pure Welsh lime was available, with the result that Sulphur was very appreciably eliminated during the blow; but on one or two occasions, when impure local lime was employed, owing to non-delivery of the usual material, considerable trouble was experienced with the increase of Sulphur in the finished steel.

It may be taken as generally admitted, that a fluid calcareous slag is the main factor in the elimination of Sulphur, while the fact that a certain amount of Sulphur passes out of the metal after the addition of the Ferro-Manganese, shows that Manganese plays some part in the elimination. Whatever the reaction is, it is probable that the Manganese which passes to and from the slag during the after-blow, as shown by Wedding, assists in the removal of the Sulphur. It may be a direct reduction of the Ferrous Sulphide by the Manganese, with formation of the Sulphide of Manganese, this being assisted by the fluid calcareous slag; or it may be an indirect reaction, the Manganese Oxide formed increasing the fluidity of the slag, and enabling the calcareous slag to act more effectively on the metal. So far as the author is aware, no direct experimental evidence elucidating the particular reaction in the converter can be adduced. We know that in the metal mixer Sulphur is directly eliminated as Sulphide

* *Mittheilungen aus den Königl. technischen Versuchsanstalten zu Berlin*, 1893, p. 28, et seq.

† *Iron and Steel Inst. Journ.*, 1893, vol. i., p. 90, et seq.

of Manganese, on the addition of Manganiferous iron to high Sulphur iron, and this distinctly supports the hypothesis of removal as Sulphide of Manganese. On the other hand, there is considerable evidence that by increasing the fluidity of a calcareous slag, the removal of Sulphur is effected apart from the presence of Manganese.

Phosphorus.—In the early days of the basic Bessemer process, pig-iron containing from 1·5 to 2 per cent. of Phosphorus was frequently used, but as the metal had necessarily to be low in Silicon, it was soon found that, even with the greatest care, there was considerable risk of the metal becoming too cold for tapping, and the loss from skulling was considerable, consequently a more Phosphoric pig-iron was soon generally adopted. To obtain the necessary heat in the finished metal, with pig-iron containing 0·5 per cent. of Silicon, the Phosphorus should not be less than 2·5 to 3 per cent.—preferably the latter—and in some works pig with 3·5 to 3·8 per cent. of Phosphorus has been regularly used without in any way deteriorating the quality of the finished steel.

As the Phosphorus is not appreciably removed until all the other impurities have been eliminated, the heat from its oxidation is concentrated at the end of the blow, when it is most required, and thus it compensates for the absence of Silicon, the great heat producer in the acid Bessemer.

The curves in fig. 87, taken from Wedding, together with general curves on p. 94, show the rate of oxidation of the Phosphorus in pig-irons containing different percentages of this element, and it will be seen that only about 10 per cent. is, on an average, removed before the after-blow commences. It cannot, of course, be assumed, in view of the strong affinity which Phosphorus has for Oxygen, that the Oxygen of the blast, or the Oxide of Iron formed, especially selects the Silicon, Carbon, and Manganese for oxidation during the first part of the blow, and then attacks the Phosphorus. There can be little doubt that the Phosphorus is oxidised from the commencement of the operation at the same time as the other elements, but that in the absence of a basic fluid slag rich in lime, the Phosphate of Iron is immediately decomposed in the presence of an excess of iron containing Carbon. Stead* in 1879, by a very pretty experiment, showed clearly that this was so.

He melted Cleveland pig in a large lime-lined crucible, impinged upon the surface a jet of air, and as the Oxide was formed, he absorbed it with a lump of lime, and found it to consist largely of Phosphate of Iron. When the blast was stopped, the surface of the metal rapidly cleared, the Oxide and Phosphate of Iron being reduced by the Carbon in the metal, before it could reach the sides of the crucible to be absorbed by the lining, and it was only when the metal was practically decarburised that the Oxide formed on the surface ceased to be reduced.

In the Bessemer converter, Phosphate of Iron is formed near the twyers, but in passing through the bath of metal, it is reduced by the Carbon, Silicon, &c., in the mass of metal before it can reach the slag. Stead found that it was impossible to dephosphorise to the slightest extent at the high temperature existing in an acid Bessemer converter, even when over-blowing was continued for fifteen minutes, but if lumps of ferruginous slag, containing over 50 per cent. of Oxide of Iron and 39 per cent. of Silica, were stirred into fluid Cleveland pig-iron, 50 per cent. of the Phosphorus was removed, showing that temperature was a very important factor effecting the reaction.

Sir Lowthian Bell, in 1878, by running metal into a bath of molten Oxide of Iron in a furnace lined with "Blue Billy," demonstrated most clearly that at comparatively low temperatures Oxide of Iron was capable of removing

* *Proceed. Inst. Cleveland Engineers*, 1879, p. 62.

the greater part of the Phosphorus from pig-iron, the Carbon being removed only to a small extent. The actual results obtained were the removal of 95 per cent. of Silicon, 84 per cent. of Phosphorus, and only 11 per cent. of

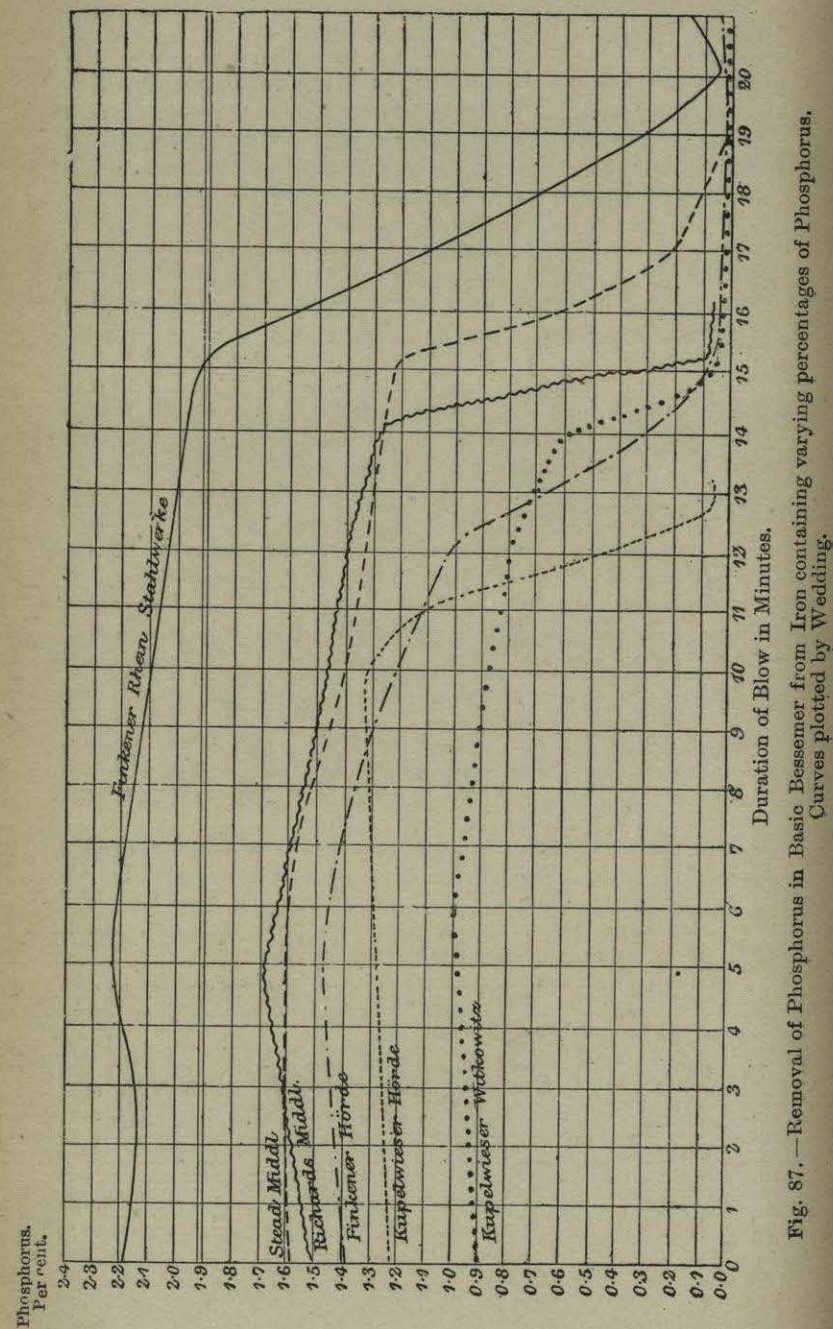


Fig. 87.—Removal of Phosphorus in Basic Bessemer from Iron containing varying percentages of Phosphorus. Curves plotted by Wedding.

Carbon. In this particular experiment there were conditions similar to those prevailing in the basic Bessemer during the early part of the blow,

except that in the latter case the temperature is higher, and the proportion of Oxide of Iron to metal less.

There seems little doubt that if it were possible to keep the temperature of the converter metal only slightly above that of molten pig-iron, dephosphorisation would result from the commencement of the blow, or, at all events, as soon as the Silicon was removed and sufficient Oxide produced in excess to form Phosphate of Iron. Owing, however, to the high temperature prevailing, any Phosphate of Iron formed is reduced by the metallic bath, sufficient lime not being dissolved in the slag to combine with and hold it. Towards the end of the blow, the conditions as regards basicity of slag are changed, as with increasing temperature the slag increases greatly in fluidity and absorbs more lime. After the removal of Carbon, Silicon, and Manganese, the metal bath is more readily oxidised, with the result that the large excess of Oxides of Iron and Manganese rapidly oxidises the Phosphorus; and the Phosphate of Iron thus formed, being brought into intimate contact with a very fluid slag, rich in lime, gives up its Phosphorus to the latter, with the production of a Phosphate of Lime,* a compound which is not appreciably reduced by metallic iron at the temperature of the converter. It has been shown by Messrs. Hilgenstock, Stead, Ridsdale, and others, that the Phosphoric acid exists in the slag in combination with four atoms of lime to one of Phosphoric Acid—that is to say, as tetrabasic Phosphate of Lime, $4\text{CaOP}_2\text{O}_5$; but to ensure the formation of a stable Phosphate, it is necessary that lime should be present considerably in excess of that theoretically required to form this Phosphate.

Rephosphorisation of Metal on Addition of Spiegel, &c.—On adding Spiegeleisen or Ferro-Manganese at the end of the blow, it is found that the Phosphorus is to some small extent reduced from the slag, and passes back into the metal, so that it is practically impossible to make high Carbon steel by means of additions of Spiegeleisen in the converter. The difficulty is overcome to some extent by pouring off the great bulk of the slag before making the Manganese additions, or by adding the latter in the ladle, the slag being kept back as much as possible in the converter during pouring. Different explanations have been given of the reason of this reduction, it being generally held to be due to the CO given off, and to the reducing action of the Manganese itself.

Stead, on heating basic slag at a very high temperature in an atmosphere of Carbon Monoxide, obtained buttons of iron free from Phosphorus, showing that the iron, but not the Phosphorus, had been reduced. Again, on simultaneously melting equal quantities of Ferro-Manganese and carburetted iron in separate crucibles in the same furnace with similar proportions of Phosphate of Lime, he found that the button of metal obtained from the Ferro-Manganese contained 1.0 per cent. of Phosphorus, that from the carburetted iron only 0.1 per cent. In another experiment, by increasing the length of time in the furnace, he obtained a Ferro-Manganese button containing as much as 5 per cent. of Phosphorus.

The heat of formation of Phosphide of Manganese is considerably greater than that of Phosphide of Iron, and consequently we should expect that Manganese would be a more powerful reducing agent than iron for Phosphate of Lime.

These experiments seem to point very strongly to the probability that Manganese acts as a direct reducing agent on the Phosphoric

* Stead has shown that when Phosphate of Iron and Lime are heated together, Phosphate of Lime and Oxide of Iron are obtained. *Proceed. Inst. Cleveland Engineers*, 1879, p. 59.

Acid in the slag, and that the Carbon Monoxide given off takes little part in the reduction, although by agitating the bath and bringing metal and slag into intimate contact it assists indirectly. It has been mentioned that Stead found that Phosphide of Iron would reduce Oxide of Manganese, and that this Oxide is certainly reduced during the Bessemer blow from the slag. Consequently, if the above reaction takes place, Manganese then is acting, on the one hand, as a reducing agent, and Oxide of Manganese acting under similar conditions as an oxidising agent and being itself reduced. Although the conditions during the after-blow and at its finish are similar, they are by no means identical, and the difference in temperature, together with the Silicon in the Ferro, and the presence of the reducing Carbon Monoxide gas given off, may constitute just sufficient variation to cause a reversal of the chemical reaction, a phenomenon which in many other cases is simply a matter of temperature. Whatever the exact cause of this reduction of Phosphorus, it cannot be entirely prevented, but it may be largely reduced by maintaining a very calcareous slag, as the more basic the slag, the less readily will the Phosphoric Acid be removed from it.

Re-carburisation in the Basic Bessemer Process.—Owing to the tendency to over-oxidation during the basic after-blow, somewhat larger quantities of Ferro-Manganese or Spiegel are required than in a corresponding acid blow, and numerous attempts have been made to decrease this by adding carbonaceous matter in various forms to reduce the excess of Oxides before adding the Ferro-Manganese. Basic material mixed with tar and other carbonaceous matter, made into compact bricks by coking, and wooden boxes filled with carbonaceous matter and pig-iron to weight them have been tried, but not generally adopted. Grey hematite previously heated to a red heat, in the case of soft steel, is frequently used, and probably this is about the best practice and is the one most generally followed. The use of a good manganiferous pig-iron for blowing is the best method for reducing the quantity of finishing metal required, as when this is used some Manganese, often as much as .2 or .3 per cent., is left in the metal at the end of the blow, and tends greatly to reduce the over-oxidation. In the case of rail steel, when Carbon from 0.35 to 0.45 per cent. is required, Spiegel melted in a small cupola and run into the ladle, or else some modification of the Darby process (p. 189) of recarburising is employed. The economy of using the latter for these comparatively low Carbon steels is more apparent than real, since 15 per cent. Spiegel can now be bought at practically the price of rail steel. As every cwt. added to the charge contains 94 per cent. of mixed metals, Iron and Manganese, this means so much more weight in the ingots; whereas, when Carbon only is added, although the actual cost of material is practically nil, the increase in weight only equals the percentage of Carbon actually absorbed. The percentage of iron in the slag is a matter which, in many works, does not receive the attention which it deserves, but it is a most important point, and furnishes a very good indication as to whether the operation of blowing is being conducted with care. In a works producing 500 tons of slag per week, an increase of Oxide of Iron equal to 2 per cent. of iron in the slag means a loss of 10 tons of steel, which, at a very low estimate, is equal to £30 per week, and this is very likely to occur if the working of the process is not controlled by frequent analyses of the slag, and every precaution taken to keep the amount of Oxide present as low as possible. The amount of Oxide of Iron in the basic slag at the end of the blow should not, as a rule, exceed 13 per cent., equal to about 10 per cent. of metallic iron.

Effect of Oxide Additions.—It has already been pointed out that it is most important to obtain a fluid slag as early as possible in the blow, and, if in addition to this, the yield per ton of pig-iron used can be increased, two very important points will have been gained. This may to some extent be effected by adding easily fusible Oxides of Iron with the lime before putting the metal into the converter, when there is little doubt that a considerable proportion of such Oxides is reduced by the metalloids in the pig-iron, in the same way that the Oxides formed at the twyers are reduced. In some works as much as 10 cwts. of Oxide are added to a 7-ton charge, without the resulting slag containing any more iron than in similar charges blown without such additions, and it is not an unusual practice to add 1 cwt. of Oxide per ton of metal, part with the first lot of lime, and part just before the after-blow. The advantage of adding some Oxide just before the after-blow is that the fluidity of the slag is increased, and this tends to shorten the after-blow, and also to remove the Phosphorus more completely. The objection to doing this is that there is a possibility of obtaining an oxidising slag which tends to produce red-short metal, unless larger additions of Ferro are made; but this view does not seem to have been borne out by experience. It is important that the Oxides added should be non-silicious, and good mill-furnace cinder from basic slag, or Oxide bottoms, answers admirably, and may be mixed with mill or hammer scale.

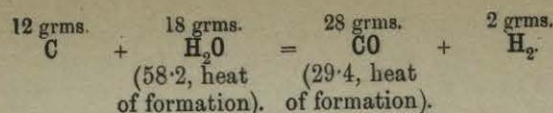
Thermo-Chemistry of the Acid and Basic Bessemer Processes.

All chemical action is accompanied by a redistribution of energy in the reacting bodies. Some of this energy takes the form of heat, and as the amount of heat liberated and absorbed during any reaction is invariable, and can be measured, the thermal aspects are as important in some respects as the chemical and physical aspects. When two bodies, such as Carbon and Oxygen, combine to form Carbon Monoxide (CO) or Carbon Dioxide (CO₂), a certain number of heat units are evolved; and when the CO or CO₂ is dissociated or split up again into its two elements, Carbon and Oxygen, the same number of heat units are absorbed. In general terms, a heat unit may be defined as the amount of heat required to raise a given weight of water through a given temperature. The weight of water taken in the following calculations is 1 kilogramme* of water from 15° C. to 16° C., and when 50 heat units are said to be evolved it means that sufficient heat has been developed to raise 50 kilogrammes of water from 15° C. to 16° C. This heat unit is termed a Calorie. When Carbon and Oxygen combine in the proportion of their chemical equivalents to form CO₂, we have 12 parts of Carbon uniting with 32 of Oxygen, and when 12 grammes of Graphite are burned to CO₂ it has been found experimentally that the evolution of heat is 97.6 calories, so that this reaction may be expressed by the following equation:— $C + O_2 = CO_2 + 97.0$ heat units or calories.

Here 97.6 heat units are evolved or given out, and this is termed an *exothermic* reaction—that is to say, the heat disturbance is positive, and this, in equations, is denoted by a + sign.

If, on the other hand, we oxidise Carbon by means of steam, as is done in making water-gas, the total result of the reaction is an absorption of heat; and if heat is not supplied from an independent source the reaction ceases, thus—

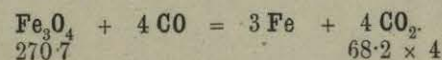
* Some writers base the calorie on 1 gramme of water, and call it "therm"; but the kilogramme calorie is used as more convenient for our purpose.



That is to say, there are 29.4 heat units evolved by the combustion of Carbon to CO—58.2 units absorbed in splitting up the water into O and H, so that the final result is that there is a loss of 28.8 heat units, which explains why it is necessary to supply heat by forcing air into a water-gas producer after steam has been oxidising the Carbon for a few minutes. This reaction, then, and all those which are attended with absorption of heat, are termed *endothermic*, and the result of the redistribution of heat is denoted by a - sign.

In considering these heat reactions the physical state of the bodies reacting, and also that of the products, whether solid, liquid, or gaseous, must be taken into account, and also the temperature at which the reaction takes place. This latter is important to remember, as a reaction which at one temperature may be attended with an evolution of heat may at another temperature result in heat being *absorbed*. Thus CO in burning to CO₂ at a comparatively low temperature evolves 68.2 heat units, but at a temperature approaching 3,000° C. only 37.0 heat units, and if we consider the reduction of Fe₃O₄, or Magnetic Oxide of Iron, by CO at a low and high temperature respectively, we get the following.—

The heat of formation of Fe₃O₄ is 270.7 heat units—that is to say, that three equivalents of Iron (56 × 3 = 168 grammes), on being oxidised to Fe₃O₄, evolve 270.7 heat units, and consequently 270.7 units will be absorbed when it is reduced. Carbon Monoxide (CO) in burning to CO₂ evolves 68.2 units at low temperatures. Then

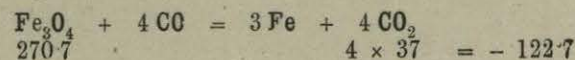


In the reduction of Fe₃O₄ we get 270.7 units or calories absorbed, or - 270.7 units evolved. In burning 4 CO to 4 CO₂ we get 68.2 × 4, or 272.8 units.

Therefore the final result is

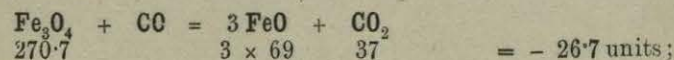
$$272.8 - 270.7 = 2.1 \text{ heat units evolved.}$$

This is an exothermic reaction, and is denoted by + 2.1. If we consider the same reaction at temperatures near 3,000° C., the heat absorption by dissociation of Fe₃O₄ is the same, but the heat evolved by oxidation of CO to CO₂ is only 37 units instead of 68.2 units. Thus



shows a deficiency of 122.7 units.

If we assume that the iron is reduced to Ferrous Oxide only, the equation becomes

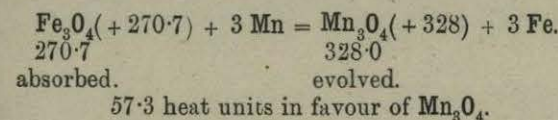


so that the reaction is still attended by an absorption of heat.

These reactions would then be endothermic, and this explains in part how reactions are reversible, a reducing action at one temperature ceasing to be so, and even becoming an oxidising one at another. Chemical reactions take place only within certain limits of temperature, which vary with the par-

ticular substances. Thus Carbon and Oxygen do not combine at ordinary atmospheric temperatures, and at extremely low temperatures even the most energetic of chemical actions practically cease. On the other hand, at extremely high temperatures most chemical compounds are dissociated.

On the heat of formation of a compound—that is to say, on the number of heat units evolved at its formation or which will be absorbed on its dissociation—will depend its stability when brought into contact with another body under conditions in which they can react upon each other. Thus an oxidised compound will resist or undergo reduction when brought into contact with a reducing agent, according as its heat of formation is greater or less than the heat of formation of the body which would result from its reduction. For instance, Manganese is able to reduce Magnetic Oxide of Iron, because the resultant Manganese Oxide has a greater heat of formation than the Oxide of Iron.



This enables the action of Ferro-Manganese as a deoxidising agent to be understood.

These theoretical considerations have a very important bearing on the reactions taking place in the Bessemer and Siemens processes, and serve to explain why certain bodies are more readily oxidised than others, and form stable compounds in the slag, thus allowing the impurities to be removed from the iron. The heat developed is the heat evolved, as the result of chemical combination, minus any heat absorbed by the reduction of bodies added to bring about such oxidation. In the case of the Bessemer process, the oxidising agent is the free Oxygen of the air, and, consequently, if we assume for the present that the Carbon, Silicon, Sulphur, &c., &c., in the pig-iron are dissolved in the iron, and not in any way combined, the heat developed will be the sum of the heat units evolved by the oxidation of the impurities present. In the case of the Open Hearth or Siemens process, the oxidising agent after the bath is melted is the Oxide of Iron added, and the heat units finally produced will be the same as in the Bessemer process (assuming the composition of the bath to be the same), minus the heat units absorbed in reducing the Oxide of Iron. It is true that in the Bessemer process Oxide of Iron acts to a large extent as the oxidising agent; but this Oxide is formed at the tuyers with evolution of heat, and exactly the same amount of heat is re-absorbed when it is dissociated and gives up its Oxygen to the impurities present, so that there is no loss, and the Oxide simply acts as an agent for conveying Oxygen to the bath. In calculating the actual heat developed in the Bessemer process, it is of course necessary to deduct the number of heat units carried away by the products of combustion, loss by radiation, &c., but, at best, only an approximation to the loss from these sources can be arrived at. The loss by radiation is fairly constant for all qualities of iron, if blown for the same length of time, and it is usual to neglect it altogether.

It is by no means necessarily correct to assume that the Carbon, Silicon, Sulphur, Phosphorus, Manganese, &c., exist in the free state in iron at high temperatures, as Carbides, Silicides, and Phosphides of Iron are well known. If these bodies are in chemical combination with the iron, they must, before they can be oxidised, be decomposed with absorption of heat, and such heat must be deducted from that evolved on their oxidation. Before, however, discussing the somewhat complex

question of the constitution of the pig-iron, it may be advisable to give the method of calculating the heat evolved on the assumption that the elements exist in the free state, and afterwards further consider the question in the light of more recent investigation.

The following data are necessary, so that an allowance may be made for the heat carried away by the products of combustion:—

Specific Heats: C = 0.241; CO = 0.2479; O = 0.218; H = 0.244; FeO = 0.17; molten pig-iron = 0.110; molten steel = 0.16; the two latter values being only approximations. The initial temperature of the molten pig-iron is 1,400° C., and the average temperature during the blow 1,700°. The air is supposed to be dry, so no correction is made for moisture. The composition of the pig-iron is assumed to be as follows:—

C = 3.5 per cent.; Silicon = 1.0 per cent.; Manganese = 1.5 per cent.; Phosphorus = 3.0 per cent.; 2 per cent of the iron will be burnt to FeO, according to Campbell's estimate.* For convenience of calculation, we may assume 1,000 kilos. to be blown.

The following are the heats of oxidation:—

| | | Heat Units or Calories. | |
|--|------------|----------------------------|----------|
| Si + O ₂ , i.e., 28 grms. of Si combining with 32 grms. O | | | = 179.6. |
| C + O, " 12 " C | " " " 16 " | | = 29.4. |
| S + O ₂ , " 32 " S | " " " 32 " | | = 69.3. |
| P ₂ + O ₅ , " 62 " P | " " " 80 " | | = 365.2. |
| Mn + O, " 55 " Mn | " " " 16 " | | = 91.0. |
| Fe + O, " 56 " Fe | " " " 16 " | | = 69.0. |
| Fe ₃ + O ₄ , " 168 " " | " " " 64 " | | = 270.7. |

| Heat developed from one kilogram of element. | Heat developed from one kilogram of element. |
|--|--|
| C, 2,450 | Mn, . 1,654 |
| Si, 6,414 | Fe, . 1,232 (Ferrous Oxide formed). |
| S, 2,166 | Fe, . 1,611 (Magnetic Oxide formed). |
| P, 5,890 | |

In 1,000 kilos. of metal of the above composition we have 35 kilos. of Carbon, 10 kilos. of Silicon, 15 kilos. of Manganese, 30 kilos. of Phosphorus, and 20 kilos. of iron to be oxidised, and thus the total heat evolved will be, in round numbers—

| | Heat Units or Calories. |
|----------------------------------|-------------------------|
| Carbon, 2,450 × 35 | = 85,750 |
| Silicon, 6,414 × 10 | = 64,100 |
| Manganese, 1,654 × 15 | = 24,800 |
| Phosphorus, 5,890 × 30 | = 176,700 |
| Iron, 1,232 × 20 | = 24,640 |
| Total heat evolved, | = 375,990 |

From these heat units must be deducted the heat units carried away in the gaseous products of combustion, and in the Nitrogen which passes away with them, and, also in the case of solid products of combustion, the heat absorbed in raising them to the temperature of the bath. It is assumed, for the purposes of calculation, that all the Carbon is burnt to CO, although, according to Snelus, about 17 per cent. is burnt to CO₂.

35 kilos. of Carbon require 46.7 kilos. of Oxygen, and produce 81.7 kilos. of CO. This necessitates the introduction of $\frac{46.7 \times 77}{23}$ kilos. of Nitrogen.

* *Structural Steel*, p. 73.

Therefore, the heat absorbed will be—

| | |
|---|---|
| By Carbonic Oxide, | 1,700 (81.7 × 0.2479) - (35 × 0.241) 1,400 = 22,600 calories. |
| By accompanying Nitrogen, | $\frac{46.7 \times 77 \times 1,700 \times 0.244}{23} = 64,800$ " |
| By O for oxidation of Silicon to SiO ₂ , | 11.43 × 0.218 × 1,700 = 4,200 " |
| By accompanying Nitrogen, | $\frac{11.43 \times 77}{23} \times 0.244 \times 1,700 = 15,800$ " |
| By O for oxidation of Manganese to MnO, | (4.364 × 0.218 × 1,700) + $\frac{4.364 \times 77}{23} \times 0.244 \times 1,700 = 7,600$ " |
| By O for oxidation of Phosphorus to P ₂ O ₅ , | (38.7 × 0.218 × 1,700) + $\frac{38.7 \times 77}{23} \times 0.244 \times 1,700 = 68,000$ " |
| By O for oxidation of iron to FeO, | (25.7 × 0.17 × 1,700) - (20 × 0.11 × 1,400) + $\left(\frac{5.71 \times 77}{23} \times 0.244 \times 1,700\right) = 12,300$ " |
| | Total heat absorbed, 195,300 " |

The heat remaining in the converter is, therefore, 375,990 - 195,300 = 180,690 calories.

Although the foregoing statement gives a general idea of the heat produced during a Bessemer blow, it is necessary to consider the view advanced by Professors Ponthière and Hartley, and other chemists and metallurgists as to the constitution of molten iron. Various Carbides, Silicides, and Phosphides of both iron and Manganese are well known, and the calculations of both Professors Ponthière and Hartley, on reactions in the Bessemer converter, are based on the assumption that some of the more stable of these exist in iron at the temperature of the Bessemer converter.

The researches of Troost and Hautefeuille* have shown that the Carbide, Silicide, Sulphide, and Phosphide of Manganese evolve a considerable amount of heat at the moment of formation, or, in other words, are stable bodies, while the corresponding iron compounds, with the exception of the Phosphide, are comparatively unstable. On this account we may assume that the Manganese exists in the pig-iron almost entirely as Carbide, Silicide, and Sulphide, and none in the free state. The Phosphides of Iron and Manganese are both stable bodies, so in this case we may assume that the Phosphorus is distributed between the iron and Manganese in the ratio of their masses—i.e., practically all combined with the iron. The fact that both the Carbide and Silicide of Manganese are stable bodies, and that, as a rule, there is not sufficient Manganese present to combine with all the Carbon and Silicon, leaves us in doubt as to how these two elements are combined. Professor Ponthière† considers that we are justified in supposing that two-thirds of the Manganese is in the form of Carbide and one-third as Silicide, this being about the ratio of their respective heats of formation. The rest of the Carbon and Silicon will be combined with the iron. Carnot and Goutal‡ have also studied the constitution of cast iron, and have come to the following conclusions:—Sulphur is usually combined with Manganese as MnS, any excess being combined with the iron as FeS.

* *Annales de Chimie et de Physique*, 5th series, vol. ix., 1876.

† *Iron and Steel Inst. Journ.*, 1897, vol. ii.

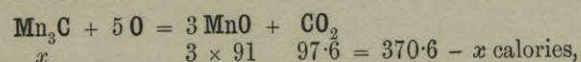
‡ *Annales des Mines*, vol. xviii., pp. 263-300.

Phosphorus is combined directly with iron as Fe_3P . Silicon is usually free, but it can combine with Manganese and with iron, forming MnSi and FeSi respectively, the latter, however, is decomposed on slow cooling. Carbon is combined with both Manganese and iron, probably as $4\text{Fe}_3\text{C}$, Mn_3C , any excess of Carbon being combined with iron, forming Fe_3C .

On the above assumption, the constitution of the pig-iron that we have been considering would be as follows:—

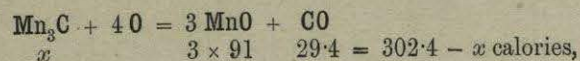
| Pig-Iron Analysis. | | Constitution of Molten Iron. | | |
|--------------------|------------------------|------------------------------|--|-----------|
| Per cent. | | | Per cent. | Per cent. |
| C = 3.50 | Carbide of Manganese, | Mn_3C , | $\left\{ \begin{array}{l} \text{Mn} = 1.00 \\ \text{C} = 0.07 \end{array} \right\}$ | 1.07 |
| Si = 1.00 | Silicide of Manganese, | MnSi , | $\left\{ \begin{array}{l} \text{Mn} = 0.50 \\ \text{Si} = 0.25 \end{array} \right\}$ | 0.75 |
| S = 0.02 | Phosphide of Iron, | Fe_3P , | $\left\{ \begin{array}{l} \text{Fe} = 16.26 \\ \text{P} = 3.00 \end{array} \right\}$ | 19.26 |
| P = 3.00 | Carbide of Iron, | Fe_3C , | $\left\{ \begin{array}{l} \text{Fe} = 46.34 \\ \text{C} = 3.31 \end{array} \right\}$ | 49.65 |
| Mn = 1.50 | Silicide of Iron, | FeSi , | $\left\{ \begin{array}{l} \text{Fe} = 1.50 \\ \text{Si} = 0.75 \end{array} \right\}$ | 2.25 |
| | Sulphide of Manganese, | MnS , | Traces | |
| | Free Iron, | ... | | 27.02 |
| | | | | 100.00 |

The heat developed by the oxidation of these compounds may be calculated in the following manner:—For the oxidation of Manganese Carbide the thermal equation is—



or 370.6 calories, if x , the heat of formation of the Carbide, be zero.

If it is assumed that the Carbon is burnt to CO instead of CO_2 , we get—



or 302.4 calories when $x = 0$.

In the same way we arrive at the following values of the heats of oxidation of the various constituents of the iron, assuming for the moment that the heat required to decompose them, or, in other words, their heat of formation is zero:—

TABLE XVII.—HEATS OF OXIDATION.

| | |
|---|-------|
| Carbide of Manganese (burnt to CO_2), | 370.6 |
| " " (burnt to CO), | 302.4 |
| Sulphide " " | 160.2 |
| Silicide " " | 270.6 |
| Phosphide of Iron, | 129.9 |
| Carbide of Iron (C burnt to CO_2), | 101.5 |
| " " (C burnt to CO), | 78.8 |
| Sulphide of Iron, | 138.2 |
| Silicide of Iron, | 248.6 |

In every case these values refer to a *gram-atom* of the metal. In order to arrive at the *true* heats of oxidation we must subtract from them the heats of formation of the various compounds. Unfortunately these heats of formation are not accurately known in many cases. The following table,

slightly altered from one by Professor Ponthière, gives approximations sufficiently close for the present purpose:—

TABLE XVIII.—HEATS OF FORMATION.

| | | |
|------------------------|-------------------------|-----------------|
| Carbide of Manganese, | Mn_3C , | 114.4 calories. |
| Sulphide of Manganese, | MnS , | 53.4 " |
| Silicide of Manganese, | MnSi , | 47.4 " |
| Phosphide of Iron | Fe_3P , | 43.3 " |
| Silicide of Iron | FeSi , | negligible. |
| Carbide of Iron, | Fe_3C , | negligible. |

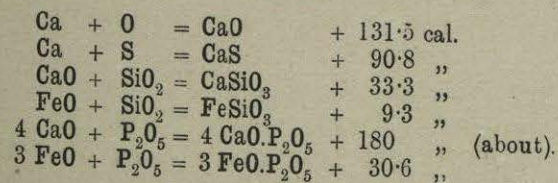
Subtracting these values from the values calculated on the assumption that the heats of formation are zero, we arrive at the results given in the following table:—

TABLE XIX.—HEATS OF OXIDATION OF THE CONSTITUENTS OF IRON.

| | Formula. | Heat of Formation. | Heat of Oxidation per gram-atom of free metal. | Heat of Oxidation of Compound per gram-atom of the metal in combination. |
|---|-----------------------|--------------------|--|--|
| Silicide of Iron, | FeSi | Negligible | 248.6 | 248.6 |
| Carbide of Manganese (C burnt to CO_2), | Mn_3C | 114.4 | 370.6 | 256.2 |
| Sulphide of Iron, | FeS | 24.0 | 138.2 | 114.2 |
| Sulphide of Manganese, | MnS | 53.4 | 160.2 | 106.8 |
| Silicide of Manganese, | MnSi | 47.4 | 270.6 | 223.2 |
| Carbide of Iron (C burnt to CO_2), | Fe_3C | Negligible | 101.5 | 101.5 |
| Phosphide of Iron, | Fe_3P | 43.3 | 129.9 | 86.6 |
| Carbide of Iron (C burnt to CO), | Fe_3C | Negligible | 78.8 | 78.8 |
| Carbide of Manganese (C burnt to CO), | Mn_3C | 114.4 | 302.4 | 188.0 |

In the above table it has been assumed that the iron is burnt to Ferrous Oxide. This is certainly true to a large extent as will be shown, although the burnt metal contains Magnetic Oxide. In any case, the substitution of Magnetic Oxide for Ferrous Oxide would make only a slight difference to the above values.

To arrive at an accurate estimate of the heat evolved during oxidation, it would be necessary to add to the above the heat developed by the formation of the slag. In many cases the required data are wanting, and even the specific heat of the slag has not been determined. The following figures, however, are available:—



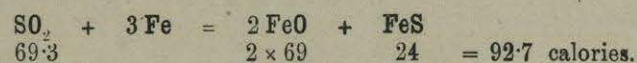
In view of the complex constitution of pig-iron at high temperatures, and the lack of exact knowledge of the form in which the foreign elements exist in it, the thermal calculations given above must be considered as an approximation only. Whether the elements exist in anything like the com-

bination suggested by Professor Ponthière, or by Carnot and Goutal, in the present state of our knowledge it is impossible to say, but we may, for the purposes of calculation, assume that they exist in some such form of combination, and therefore from any heat evolved must be deducted that absorbed in decomposing such compounds. In view of the progress which is being made in the analysis of pig-iron and other alloys, especially in respect to their ultimate composition, it is of importance that the student should cease to regard pig-iron as mere mixtures of Carbon, Silicon, Manganese, &c., with metallic iron, but should accustom himself to think of these elements as forming definite compounds with the iron.

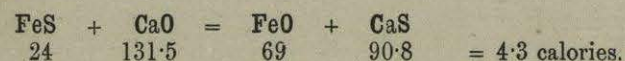
The amount of heat evolved and absorbed by the decomposition and oxidation of the impurities in the Siemens process is the same as for the Bessemer process, but the total heat produced in the bath from metal of the same composition is less, owing to the oxidation being effected by FeO or Fe₂O₃, which has to be reduced with consequent absorption of heat; it must be remembered that the heat produced by the oxidation of the impurities is spread over some hours instead of being all evolved in a few minutes. On the other hand, no heat is carried away by Nitrogen passing through the molten metal as in the Bessemer process.

The foregoing calculations derive real interest and importance from the fact that they enable us to give a reasonable explanation of many of the reactions occurring during the manufacture of steel by the Bessemer and Siemens processes.

Let us first consider Sulphur. It is well known that Sulphur is not removed during the acid-blow or in acid Siemens practice, and its removal is very irregular during the basic-blow and in basic Siemens practice. When Oxygen is blown through a bath of iron containing FeS, we should expect that FeO and SO₂ would be formed, and that the latter would pass away with the products of the combustion; but the reason why this does not take place is shown by the following equation:—

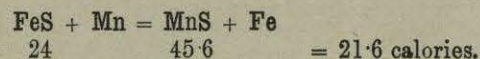


Thus assuming SO₂ to be formed, it would immediately be reduced by the Fe and FeS re-formed, as its reduction is attended by the gain of 92.7 calories. If, however, we have lime present, the following reaction *may* take place:—



This reaction, while exothermic, is very feebly so, and it explains why the removal of Sulphur, even under basic conditions, is very erratic.

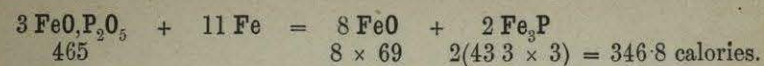
It is also well known that the addition of Manganese does, under certain conditions, remove the Sulphur, or at all events mask its effects, and it is conceivable that if it remains associated with the metal it may be less injurious as MnS than in the form of FeS.



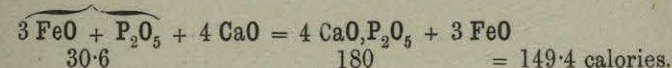
This explains the removal of Sulphur in the metal mixer as MnS.

In the case of Phosphorus in the acid converter, or acid Siemens furnace, any Phosphate of Iron formed is at once decomposed either by Silicide of Manganese, if present, or by Metallic Iron. When no Manganese is present the Metallic Iron in excess is quite sufficient to explain the reaction. The

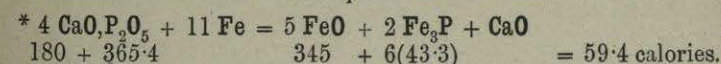
heat of formation of Ferrous Phosphate from its *elements* is 465 calories, so that we have



So that assuming that Phosphate of Iron or Phosphoric Anhydride is formed, the above thermal equation explains why it is immediately reduced with re-formation of Phosphide of Iron. If, however, we introduce a base, which, by its combination with Phosphoric Anhydride, evolves more heat than FeO, we ought to be able to replace the FeO by this base and form a more stable Phosphate. We have such a base in lime which forms a Tetra-Phosphate on uniting with P₂O₅, and evolves about 180 calories in so doing, so that we have the following reaction taking place:—



Since the lime is already oxidised when added to the bath its heat of formation need not be considered, and we have the following equation for the action of excess of iron on Phosphate of Lime:—



According to this equation, excess of iron is capable of reducing Phosphorus from the Phosphate of Lime, though the reaction is a feeble one compared with that between 3 FeO, P₂O₅ and excess of iron. It should be remembered, however, that the removal of the bulk of the Phosphorus does not begin until the Carbon and Manganese have been removed and the bath is free from these reducing agents. Its elimination is, therefore, probably due to mass action, the large excess of lime and air overcoming the reducing tendency of the free iron. We should, therefore, expect that, on stopping the blast and adding Ferro-Manganese, some of the Phosphorus would pass back, and this actually does occur to a limited extent in practice. In this connection it must be remembered that the heat formation of Phosphide of Manganese is considerably greater than that of Phosphide of Iron, and consequently Manganese would have a greater tendency than iron to reduce the Phosphorus from the slag. Although the above equations show which reactions are thermally possible, these reactions, like most others, depend largely on the temperature of the bodies reacting, and while Metallic Iron at the ordinary temperature of the Bessemer converter decomposes Phosphate of Iron, and to a less extent Phosphate of Calcium, at lower temperatures this is not the case, as is evident from Phosphorus being very largely removed, in the Bell and other washing processes, in combination with Oxide of Iron.

* It is possible that the heat of formation given—viz., 180 calories—is too low, the data for arriving at this figure not being very satisfactory.